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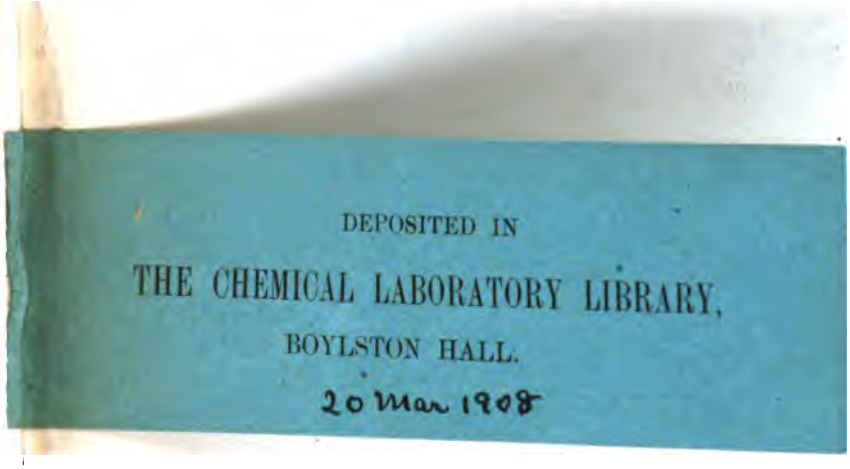
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IN ALL ITS APPLICATIONS TO

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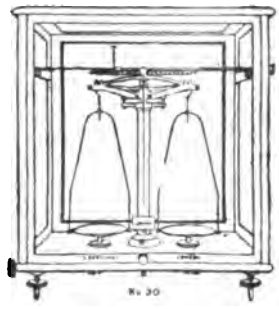

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THE ESTIMATION OF CHROMIUM IN ALLOYS.

By ARCHIBALD ALLISON.

THE usual spur to investigation, an anxiety for certitude in his results, led the present writer to examine in detail methods of estimating chromium, particularly in alloys for steel-making purposes.

The two methods most widely employed are the sodium peroxide fusion and the tribasic dry oxidation.

The first was the one in use in this laboratory, and, somewhat modified, has, in the writer's hands, given the best results.

First of all, in this method, the alloy need not be particularly finely ground, as is commonly insisted. The writer grinds till the powder just begins to cling to the agate.

Secondly, the weight taken for each estimation is always 1 grm., as this relatively large weight has been found to make for greater accuracy.

The method is briefly:—

One grm. is fused in a nickel crucible with 8 grms. sodium peroxide. The melt is extracted with about ½ litre hot water, the liquid boiled for ten minutes to expel hydrogen peroxide, and filtered. The precipitate is fused again, as before; the extraction boiled and filtered and the precipitate washed. The mixed filtrates are acidified with sulphuric acid and titrated with ferrous ammonium sulphate and potassium dichromate.

The doubtful points were:—

1. Does the filter-paper reduce the chromic acid in the hot alkaline solution?
2. Does the oxide of nickel affect the subsequent titration?
3. Is a second fusion necessary?

With these points in view, estimations were carried through side by side with varying conditions.

It was noticed that, on filtering the second extraction through paper, the first portion of the filtrate was much more yellow in colour than the whole filtrate subsequently appeared, the conclusion being that this colour was caused by the first portion of the hot alkaline liquid attacking the paper. (This must occur with the first filtration also, the actual reduction of chromic acid probably taking place on acidifying). On filtering through asbestos this phenomenon is not apparent.

In some experiments the two filtrates were mixed, acidified with sulphuric acid, and boiled with the addition of a little potassium permanganate. The liquid was then diluted to about two litres, the permanganate destroyed with 60 or 70 cc. hydrochloric acid, and boiling continued till the liquid was quite free from chlorine. The results quoted are in all cases typical.

No. of alloy.	Treatment.	Cr obtained (per cent).
1.	*a.* Filtered extractions through paper ..	62·86
	b. Filtered extractions through asbestos	62·99
2.	*a.* Filtered extractions through paper ..	63·73
	b. Filtered extractions through paper and oxidised with $KMnO_4$	63·88
3.	*a.* Filtered extractions through paper ..	62·47
	b. Filtered extractions through paper and oxidised	62·61
5.	*a.* Filtered extractions through asbestos	61·54
	b. Filtered extractions through paper and oxidised	61·54

It is thus clear that filtering through paper causes low results, which can be avoided by subsequent oxidation or filtration through asbestos.

The next experiments were carried out in the presence of the nickel.

No. of alloy.	Treatment.	Cr obtained (per cent).
6.	*a.* Fused once; boiled extraction, cooled, acidified, and titrated. The black peroxide of nickel did not completely dissolve; end-point uncertain	65·01
	b. Fused twice and filtered through asbestos	62·19
	c. Fused twice, filtered through asbestos, and oxidised with $KMnO_4$	62·12
9.	*a.* Fused once; boiled extraction, acidified, and oxidised with $KMnO_4$; end-point obscured	62·14
	b. Fused twice; filtered through asbestos	62·16

In the case of alloy No. 6*a*, the black precipitate of nickel sesquioxide obviously oxidised the ferrous sulphate to give a false result.

In the case of No. 9, the boiling dissolved up the nickel sesquioxide and prevented its oxidising effect, but, as in No. 6*a* also, the end-point was obscured by the nickel in solution combining with the ferricyanide indicator. It is therefore highly desirable to filter off the nickel precipitate.

The third point was disposed of as follows:—

No. of alloy.	Treatment.	Cr obtained (per cent).
10.	*a.* Fused once; filtered through asbestos, boiled precipitate with water containing sodium peroxide and carbonate, and filtered again.	64·34
	b. Fused twice; filtered through asbestos each time	64·37

It is thus seen that a second fusion is not strictly necessary, but most chemists would doubtless regard it as advisable.

With reference to the tribasic dry oxidation methed, the writer has obtained satisfactory results, but finds a liability for a portion of the alloy to adhere to the platinum dish very obstinately and cause low results.

Notes.—The writer takes as his standard re-crystallised potassium dichromate. The ferrous ammonium sulphate is added in the solid form. The very pure salt is re-crystallised rapidly to obtain pure small crystals, or ground to a coarse powder. This is then mixed in a large bottle and is standardised against the dichromate, portions being weighed out as required for each estimation.

The Laboratory,
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ON THE SEPARATION AND ESTIMATION OF SMALL AMOUNTS OF MANGANESE IN NATURAL SILICATES.

By PHILIP HOLLAND.

EACH year it may almost be said witnesses the birth of some process for estimating small quantities of manganese. such as are found to occur in the ashes of plants in mineral waters and in natural silicates.

Possibly the earliest of these minimetric schemes is that of Walter Crum by the lead peroxide process, and the latest that of Tarugi, who has recently observed that manganous hydroxide dissolves in glycerol and in course of its conversion to the higher oxide imparts to that solvent a ruby colour. This red colour can be made the basis of a colorimetric scheme for manganese.

It is now some eighteen years since I first began to analyse specimens of rock in order to furnish information to some of my friends who required it. In the interval many specimens have passed through my hands, and ever and anon I have felt a bit in doubt of the figure about to be recorded for the manganous oxide. Sparingly present in igneous rocks, it seemed likely that in the analytical separation some little might escape collection where it should be collected and turn up where it should not, viz., in the lime and magnesia precipitates. Manganese did at times turn up in these precipitates, and was determined colorimetrically by Crum's process, thus enabling the necessary corrections to be made.

It was the discovery of traces of manganese in the magnesian phosphate precipitate which suggested the experiments that form the subject of this article.

The sodium acetate process with double precipitation of the alumina and ferric hydroxide has always been the one employed to separate the manganese in the first instance. The further operations on the filtrate, its concentration and treatment with NH_4OH and H_2S, need no description.

The MnS precipitate requires several operations before the analyst can weigh his Mn_3O_4, for the sulphide has first to be converted to chloride, then to carbonate, and, lastly, to the oxide, which may fall short of the correct figure from loss, or be in excess of it owing to contained salts.

Seeking to abridge the process I have used the well-known reaction between manganic hydroxide and potassium iodide in the presence of slight excess of diluted chlorine-free hydrochloric acid.

The following solutions were prepared :—

1. A solution of manganous sulphate slightly acid, of which 5 cc. equalled 0·001 grm. of MnO.
2. A 10 per cent solution of pure NaOH.
3. A 5 per cent solution of pure KI.
4. Diluted HCl, equal volumes of acid and water.
5. A highly dilute solution of sodium thiosulphate.

The thiosulphate was standardised as follows :—Into a capacious flask was put 100 cc. of No. 1, and to it was added a slight excess of No. 2. The flask was then well shaken until the conversion of the manganous into manganic hydroxide was judged to be complete. Five cc. of No. 3 was next added, followed by as much of No. 4 as more than dissolved the hydroxide and rendered the solution clear of suspended particles. The contents of the flask after dilution with 150 cc. of water were then titrated with thiosulphate. This latter was so adjusted that 1 cc. equalled 0·0005 grm. of MnO under the recited experimental conditions. The thiosulphate does not for long retain its strength, but the fact is immaterial, for the operator has always at hand his manganous sulphate with which to check it. The scheme for separating the manganese from a solution, first as sulphide, and for finally estimating it indirectly as above, was tested as follows :—

Into a series of flasks was put a known amount of No. 1 along with 4 grms. of iron-free and otherwise pure NH_4Cl and 150 cc. of water at 60° C. The solutions were made ammoniacal, then saturated with H_2S, and the flasks closed and set aside for twenty-four hours. The MnS in each case was collected on a filter, and gently washed with a 5 per cent NH_4Cl solution containing a little $(NH_4)_2S$. What MnS adhered to the flask (it seldom did so) was removed by pure paper pulp, and the whole got on the filter. The wet filter next, cautiously folded, was dried and ignited in a 2½ inch Berlin crucible.

To the residue was now added ten drops of strong HCl, and the crucible gently rotated over a small flame till all oxide dissolved and Cl was quite away.

The resulting manganous chloride was put in the flask and dealt with just as for the standardising of the thiosulphate.

The following are trial experiments given in the order n which they were made.

One cc. of sodium thiosulphate equals 0·0005 grm. of MnO.

MnO taken. Mgrms.	Thiosulphate required. Cc.	MnO found. Mgrms.
10	20·1	10·05
10	19·7	9·85
5	9·6	4·80
5	9·5	4·75
5	9·8	4·90
2	3·8	1·90
2	3·6	1·80
2	4·2	2·10
2	3·4	1·70

I am disposed to attribute the slight loss which occurs to passage of MnS through the filter, or it may be that twenty-four hours' digestion with $(NH_4)_2S$ is insufficient to ensure complete precipitation of the sulphide. The scheme was now applied to the estimation of MnO in a solution made so as to simulate the filtrate from 1 grm. of some sedimentary rock after usual treatment and removal of SiO_2.

To this end I prepared a solution of the following oxides; 250 cc. of the solution represented 1 grm. of rock :

Al_2O_3	0·200
Fe_2O_3	0·080
MnO	0·002
CaO	0·009
MgO	0·024

The supposed rock would thus contain 0·2 per cent of MnO, an amount often met with in slates and shales from various geological horizons.

Taking 250 cc. of the solution, the $Al_2O_3 + Fe_2O_3$ were thrown out by acetate. The precipitate was then filtered off and washed, and re-dissolved in excess of HCl, from which it was twice thrown down by NH_4HO. The united filtrate, after concentration and complete removal of any iron it might contain, was next dealt with in the manner just described.

Thiosulphate required. Cc.	MnO found. Per cent.
3·5	0·175
3·7	0·185
3·4	0·170
3·9	0·195
Average..	0·181

So far the analyst is assumed to be working in the entire absence of Cu, Ni, Co, Zn. Should these be present he would not straightway ignite his sulphide precipitate, but would modify his operations accordingly.

In the lime and magnesia precipitates from the sulphide filtrates I could detect at times a trace of manganese. Did it pass the filter when washing the MnS in spite of all precaution?

What has been said applies to the finding of manganese in non-metalliferous rocks and in such sedimentary material as they give rise to. For those analysts whose work lies in other grooves, who perchance may be attached to a steel-works and have to determine the manganese in several specimens of steel a day, the scheme I have set forth is, in respect of time required, quite out of the question. Most steel analysts I believe treat the steel in the first instance with HNO_3, and by means of some further oxidant get their manganese in a suitable condition for titration.

Within the past three weeks I have experimented on the reaction for manganese described by Dr. Hugh Marshall in 1901 (CHEMICAL NEWS, vol. lxxxiii., p. 76). This is the now well-known persulphate reaction, whereby ammonium persulphate reacting on manganous sulphate in the presence of silver nitrate and excess of nitric acid yields permanganic acid. Marshall, discussing the reaction and its sensitiveness, suggests that a colorimetric estimation of manganese could apparently be founded upon it.

This is so, for working on the lines suggested by Dr. Marshall I have succeeded in estimating quite easily the Mn in a specimen of iron wire and in two specimens of steel. When the Mn does not exceed 1 per cent the colorimetric determination can quite well be made on half a grm. of steel. The solutions should be well diluted to, say, 500 cc. after the reaction and development of the pink colour. The $KMnO_4$ solution, wherewith to match the colour in the reaction flask, contained 0·0005 grm. of Mn per cc.

Mn per cent colorimetrically by persulphate reaction.			Mn per cent by scheme described in this article.
Iron wire.	File steel.	Steel ring.	The same iron wire.
0·92	0·37	0·87	0·92
0·89	0·35	0·91	0·95
0·91	0·32	—	0·90
0·94	—	—	0·91

The matching of dark tints in flasks when the solution, owing to its deep shade, has to measure 500 cc. is much assisted towards the close by employing two small Nessler cylinders of the same bore. In one is put 10 cc. of the solution required to be matched, and into the other 10 cc. from the matching flask. Should the tints not correspond the contents of the second cylinder are returned to the matching flask, to which a further addition of the colouring reagent is made and the operation repeated. Probably most analysts who have not some form of tintometer work so, and thus soon arrive at correct adjustment for the tint required. It may perhaps be hardly necessary to say that the volume of liquid in the flasks must be alike, also that the matching flask must also contain some of the oxidising reagents.

The development of the colour reaction between the manganous salt and the reagents should be made in a small volume of solution. The operator with a little practice soon hits on the right conduct of the process, so that the colour shall develop, gradually assume its full shade, and not be obscured by suspended silver peroxide.

London, June 25, 1907.

CHEMICAL REACTION BETWEEN SALTS IN THE SOLID STATE.*

By EDGAR PHILIP PERMAN.

IT has long been known that in a mixture of solid salts chemical reaction may take place. Experiments on the subject have been made by Spring (*vide infra*), Thorpe (*B. A. Report*, 1881, p. 580), and others. My attention was first called to the question by observing that a mixture of arsenious oxide and cadmium nitrate underwent a slow but complete change of composition, the final result being that the nitric acid was eliminated, arsenic acid taking its place.

Preliminary Experiments.—Some experiments were made in order to discover what salts would be suitable for a careful investigation. The following were selected for trial, since a chemical change could be traced by an accompanying change of colour. The salts were finely powdered but not specially dried.

Salts.	Result on mixing.
Lead nitrate and potassium iodide	Immediate action.
Lead chloride and potassium iodide	Immediate action.
Lead formate and potassium iodide	Slow action.
Lead sulphate and potassium iodide	Very slow action, colour appearing after 30 mins.
Lead oxide (litharge) and potassium iodide	No appreeiable action.
Lead carbonate and potassium iodide	No change.
Mercuric chloride and potassium iodide	Immediate action.
Mercuric cyanide and potassium iodide	No action.
Mercuric chloride and potassium chromate	Slow change.

From these salts two pairs were chosen for further study, viz., lead chloride and potassium iodide, and mercuric chloride and potassium iodide.

The salts were purified by re-crystallisation, dried over sulphuric acid, ground in a mortar, and sifted through fine silk cloth, such as is used for sifting flour; they were then kept in desiccators over sulphuric acid.

Lead Chloride and Potassium Iodide.

Effect of Drying over Sulphuric Acid.—Equivalent quantities of the salts (2 grms. potassium iodide and 1·68 grms. lead chloride) were placed in two flasks, A and B (Fig. 1), C containing concentrated sulphuric acid. The salts were occasionally warmed and shaken in order to make the drying more efficient. After standing forty-eight hours, the lead chloride was shaken from A into B, C being held in a horizontal position. The salts were mixed by shaking, when there was no apparent change of colour. The flask B, which had previously been drawn out, was then sealed off.

The mixture was watched from day to day; no change could be seen until the tenth day after mixing, when a very faint yellow colour appeared. On further keeping, the colour slowly deepened for some weeks, and then seemed to remain unaltered. In this experiment the mixture was kept in the dark.

Effect of Light.—Another mixture made in the same way, but exposed to daylight behaved in no way differently from the first.

Effect of Temperature.—On heating a similar mixture at 100° for five hours, no colour appeared, but on keeping it showed a tinge of yellow at the beginning of the third day, showing that the reaction had been much accelerated.

* A Paper read before the Royal Society, May 23rd, 1907.

Attempt to Determine the Minimum Quantity of Water necessary to Produce an Immediate Visible Reaction.

Several methods were tried:—

1. The mixture having been made in the usual way, the flask containing it was weighed, and allowed to stand open to the air on the balance pan until the yellow colour was perceptible. The increase in weight was then noted.

2. The flask containing the mixture was connected, by a ground glass joint and wide stopcock, with a small bulb containing crystallised borax. As soon as the yellow colour appeared, the bulb was detached, and the loss in weight of the borax determined.

3. The substances were dried over phosphorus pentoxide, and mixed in an exhausted globe. Measured volumes of air saturated with water vapour were then admitted until the first appearance of colour. The weight of water admitted was calculated.

The results obtained by these three methods were not very concordant, the quantity of water varying from 0·1 mgrm. to 1 mgrm. The smallest number is probably the most correct. The chief interest of the matter is in its comparison with the case of mercuric chloride and potassium iodide.

tube and contents were dried in the same way as the potassium iodide. The tube was then sealed off, and the salts were mixed by breaking the bulb.

As the result of these experiments, it was found that on mixing the salts a faint colour usually appeared at once. It was at first yellow, and changed slowly or quickly, according to the thoroughness of the drying, into the scarlet mercuric iodide. If the phosphorus pentoxide (in the pump) was of poor quality or had been much used, the red colour appeared immediately on mixing the salts, but otherwise three days were required for the full development of the colour.

With specially made phosphorus pentoxide, more complete drying was obtained, and there was no reaction. The arrangement used is shown in Fig. 2; A is the alloy septum. After introducing the salts B, B', the tube was narrowed at C, C'. The phosphorus pentoxide was then placed at D D', and the tube sealed off at both ends. Next, the phosphorus pentoxide bulbs were broken, and the whole allowed to stand for a month. The tube was then sealed off at C, C', the alloy was melted and run into E, and the salts were mixed. No colour appeared, and after keeping three years still no change had taken place; the

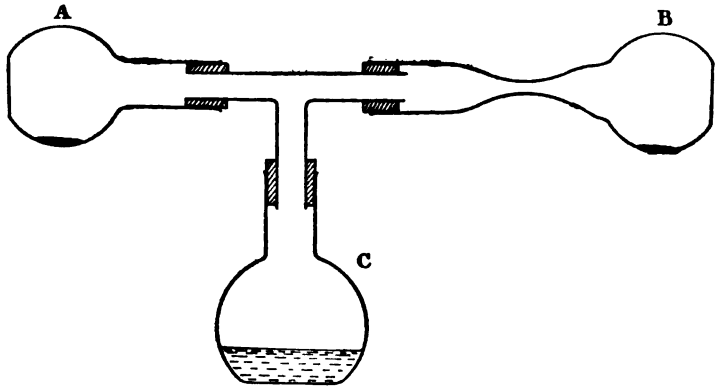


FIG. 1.

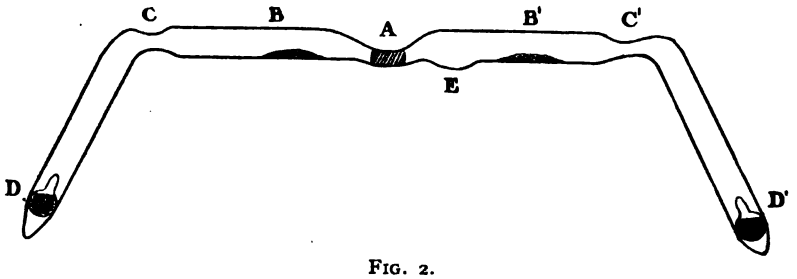


FIG. 2.

Mercuric Chloride and Potassium Iodide.

Owing to the volatility of mercuric chloride it was necessary to dry the salts separately, for otherwise some of the mercuric salt was driven over into contact with the potassium iodide. Several arrangements were used; in one a wide tube was divided by a glass septum, which was broken, after the salts were dried, by a glass rod enclosed. In another arrangement the separation was effected by a septum of fusible alloy, which was melted before mixing the salts.

The simplest device, however, was the following:—Some potassium iodide was placed in a small thin-walled bulb, and dried by gentle heating and at the same time exhausting with a mercury pump. The bulb was placed inside a wide tube closed at one end, and containing some mercuric chloride; the other end was drawn out, and the tube was then opened, when the red colour appeared. The contents of another tube, which had been kept the same time, and had accidentally contained some mercury, turned black on exposure to the air. No doubt the mercuric chloride (before drying) had been converted into a mercurous salt. The colour was the same as obtained on adding excess of potassium iodide solution to a solution of a mercurous salt.

Speed of the Reaction.—It is seen from these experiments that the reaction between mercuric chloride and potassium iodide takes place at an enormously greater rate than that between lead chloride and potassium iodide in the same conditions. The cause of the difference is at first sight not clear. The possible factors which may influence the rate of the reaction are:—(1) Quantity of water present; (2) solubility; (3) volatility; (4) degree of ionisation when

in solution. It is not necessary to consider the state of sub-division as the salts were all prepared in the same way. Solubility appears to be an important factor, for, on referring to the list of salts at the beginning of this paper, it is seen that the least soluble salts show the least action. Mercuric chloride is roughly ten times as soluble as lead chloride, but this would not account for the very great difference in the speed of the two reactions. The degree of ionisation of mercuric chloride in solution is extremely small, and this would have the opposite effect to that actually found. The volatility still remains to be considered; it is, undoubtedly, the determining factor, as shown by the following experiments:—In a wide tube constricted in the middle were placed, on one side some mercuric chloride, and on the other side potassium iodide. The tube was then sealed off, and watched from day to day. After the lapse of a month the margin of the potassium iodide was slightly coloured, and after three years the colour had travelled about 1 inch along the potassium iodide. The mercuric chloride remained free from colour. A similar experiment with lead chloride and potassium iodide showed no colour whatever. The difference was still more marked in another experiment in which the tubes were exhausted to 0·1 mm. The mercuric chloride coloured the potassium iodide *at once*, whilst after a year the lead chloride had had no effect.

Sodium Carbonate and Barium Sulphate.

In order to investigate the effect of a high temperature on reactions between solid salts, it was necessary to select those that were non-volatile. Sodium carbonate and barium sulphate were chosen; they have the further advantage that the extent of the reaction may be measured by extracting the mixture with water and estimating the sodium carbonate volumetrically.

Preliminary experiments were made in order to discover if any reaction took place during the process of extraction, and it was found that, if carried out quickly, there was no appreciable change. The following numbers were obtained:—

Na_2CO_3 taken.	$BaSO_4$ taken.	Treatment.	Na_2CO_3 found.
Grm.	Grm.		Grm.
0·454	1	Shaken with water 10 mins.	0·454
0·454	1	Allowed to stand with water 24 hours.	0·443

Effect of Heating.

Na_2CO_3 taken.	$BaSO_4$ taken.	Heated.	Temp.	Na_2CO_3 found.
Grm.	Grm.	Hours.		Grm.
0·841	1·045	5	300—400°	0·820
0·705	0·8035	35	,,	0·657

Although the temperature was considerably below the fusing-point of either salt, a marked reaction was thus found to take place. The heating was effected in a crucible without any precautions as to drying.

A mixture was then made of equivalent quantities of sodium carbonate and barium sulphate; it was ground lightly in a mortar for ten minutes, and dried over sulphuric acid. It was placed in a glass bulb at the end of a long tube, and heated in the vapour of bromnaphthalene (about 280°). The following are the results:—

Heated.	Na_2CO_3 originally present.	Na_2CO_3 found.
Hours.	Grm.	Grm.
35	0·2137	0·2155
54	0·5800	0·5831

At this temperature there is no sign of any decomposition.

The temperature of boiling sulphur (444°) was next tried. A mixture was used of two molecules Na_2CO_3 to one molecule $BaSO_4$.

	Heated.	Na_2CO_3 originally present.	Na_2CO_3 found.	Na_2CO_3 converted.
	Hours.	Grm.	Grm.	Per cent.
Series I.	20	0·5703	0·5355	6·10
	40	0·3671	0·3177	13·46
	65	0·4838	0·3971	17·92
Series II.	10	1·0224	0·9264	9·58
	16	0·8738	0·8057	7·79
	20	0·8655	0·7813	9·73
	40	0·4993	0·4581	8·25
	65	0·4970	0·4581	7·83

In the second series the mixture was somewhat drier than in the first, and the reaction appears to have ceased after a short time. The results are not very concordant, probably owing to irregularity in the quantity of moisture present.

In another series, a mixture of sodium carbonate and barium sulphate in molecular proportions was used. The salts were heated and allowed to stand over sulphuric acid before mixing. The mixture was then put into bulb tubes previously dried by exhausting with a water air-pump, and heating at the same time. The tubes were sealed, and heated in sulphur vapour.

	Heated.	$NaCO_3$ converted.	Na_2CO_3 left (calculated on total weight of mixture).
	Hours.	Per cent.	Per cent.
Series III.	10	10·92	27·84
	30	10·19	28·07
	60	11·60	27·62

Next a mixture was made of sodium sulphate and barium carbonate in molecular proportions, and was heated in sulphur vapour in order to discover whether the composition would become finally the same as in the last experiment:—

Heated.	$NaCO_3$ formed (on total weight of mixture).
Hours.	Per cent.
10	2·89
30	3·04
60	3·11

It would appear that the reaction in this direction is very much slower than in the other, and that equilibrium had not been reached; but it is impossible to say whether the two pairs of salts were in exactly the same condition with regard to moisture or not. Probably equilibrium had not been reached in either case.

Effect of Heat on a Mixture of Sodium Carbonate and Barium Sulphate in the absence of Moisture.

The substances were placed separately in a glass tube, and dried by heating and exhausting with a mercury pump. The salts were then mixed and heated fourteen hours in sulphur vapour. The result was—Sodium carbonate taken, 0·3071 grm.; found, 0·3074 grm. Thus no action takes place in the absence of moisture.

Effect of Shaking.—A mixture of 0·593 grm. sodium carbonate and 1·419 grm. barium sulphate was shaken in a closed flask for ten hours continuously. It was then found that 0·584 grm. sodium carbonate remained.

Effect of Percussion.—About 2 grms. of a mixture of two molecules Na_2CO_3 to one molecule $BaSO_4$ was placed in a heavy steel mortar with a closely fitting plunger as pestle. The latter was then hammered vigorously for thirty minutes, receiving about 900 strokes in all. On extracting with water, it was found that 4·87 per cent of the sodium carbonate had been converted into sulphate.

Effect of Pressure.—W. Spring (*Bull. Soc. Chim.*, xlvi., 166; xliv., 299) investigated reactions between sodium carbonate and barium sulphate, and between sodium sulphate and barium carbonate, under high pressures, and found that the extent of the reaction depended on the number of compressions and the time during which the mixture was left after compression.

These results were confirmed by the following experi-

ments:—A mixture of two molecules Na_2CO_3 to one molecule $BaSO_4$ was subjected in the steel mortar to a pressure of 82 tons (equivalent to 104 tons per square inch). It was then found that 1 per cent of the sodium carbonate had been converted into sulphate. It should be noted, however, that the mortar broke, so that the duration of the pressure was very short. In another experiment the pressure was 44·4 tons (56 tons per square inch, or about 8000 atmospheres), and its duration was one minute. The compressed mixture was then allowed to stand five weeks, when it was found that 4·02 per cent of the carbonate had been converted. Spring found that, after the mixture had been subjected to a pressure of 6000 atmospheres, and then left a month, 3·84 per cent barium sulphate had been converted into carbonate. It was found by Spring that mixtures of approximately the same composition were obtained, whether starting with barium sulphate and sodium carbonate or sodium sulphate and barium carbonate, thus showing that equilibrium had been attained. I have therefore confined myself to endeavouring to discover the effect of pressure on very thoroughly dried salts. The heavy mortar was first used. In order to dry the mixture, a hole was drilled sideways into the bottom of the mortar, and into this was cemented a tube containing phosphorus pentoxide. Molten wax was poured over the top of the plunger. However, the phosphorus pentoxide did not remain dry, and the result was that after the mixture had stood twenty-three days, and then been subjected to a pressure of 40 tons (equivalent to 51 tons per square inch, or 7600 atmospheres), 1·6 per cent of the sodium carbonate had been converted into sulphate.

In the next experiment the plunger passed through a rubber cork which fitted into the mouth of the mortar, and air and moisture were pumped out through the side tube. The drying was not complete owing to a slight leak and to the impossibility of shaking the powder. The result showed that 0·5 per cent of the sodium carbonate had been converted into sulphate by a pressure of 40 tons.

Owing to the difficulty of drying the salts in the heavy mortar, a lighter one was made in which the salts could be hammered, the blow of a hammer being essentially the same as a high pressure exerted for a very short time.

Effect of Percussion on thoroughly Dried Salts.—A steel mortar was made of 1¼-inch internal diameter, with a loosely-fitting piston, and the piston rod passed through a rubber cork fitting tightly into the mouth of the cylinder. Several grms. of the mixture were placed at the bottom of the cylinder, and were dried by gentle heating and shaking, and at the same time exhausting the cylinder with a Fleuss pump. The piston was then hammered vigorously for thirty minutes (about 900 strokes). On analysing the mixture it was found that only 0·1 per cent of the sodium carbonate had reacted, an amount within the limits of experimental error. An exactly similar experiment was then made without specially drying the mixture; the salts had been dried over sulphuric acid, then mixed and kept in a well-stoppered bottle. In this case 2·38 per cent of sodium carbonate was converted into sulphate. The amount converted when the heavy mortar was used (*vide supra*) was 4·87 per cent. The areas of the pistons in the two cases were approximately as 1 : 2, *i.e.*, roughly the same as the extent of the reaction.

Influence of other Solvents.

Methyl Alcohol Vapour.—Lead chloride and potassium iodide were dried separately over phosphorus pentoxide, then mixed in a special apparatus, and exposed to the action of methyl alcohol vapour, the liquid having been carefully dried by quicklime. The mixture acquired a strong yellow colour in about one hour.

Benzene Vapour.—When exposed to benzene vapour in a similar way, no change took place.

A similar experiment with mercuric chloride and potassium iodide gave a similar result, except that the mixture gradually turned black owing to the reducing action of the metallic sodium left in the tube to dry the benzene.

Chloroform Vapour.—Some lead chloride was placed at the closed end of a wide glass tube. Inside the tube two sealed thin-walled tubes were placed, one containing potassium iodide and the other pure chloroform, each previously dried by phosphorus pentoxide. The wide tube was then exhausted by the mercury pump, and sealed off. On breaking the inner tubes, there was no apparent change of colour, either when the mixture was exposed to the action of the vapour or to that of the liquid. After standing a week a faint colour appeared. (Commercial phosphorus pentoxide was used in this experiment, so that the drying was not very perfect).

Ammonia.—Some ammonia gas was dried over lime, and allowed to stand with phosphorus pentoxide (Kahlbaum's) in a glass bulb. The bulb was then sealed off, and placed, together with a small bulb containing dry potassium iodide, in a wide tube containing lead chloride. The wide tube was then heated, exhausted, and sealed off. On breaking the inner tubes, no change was observed, and after keeping for a year it was still unaltered.

With regard to the action of these solvents, methyl alcohol dissolves and ionises both salts, benzene and chloroform dissolve neither, whilst liquid ammonia dissolves and ionises potassium iodide, but forms an insoluble compound with lead chloride (*Am. Chem. Journ.*, 1898, xx., 820).

Summary and Conclusion.

1. Salts in the solid state usually undergo double decomposition when mixed (and not specially dried).

2. Reaction between solid salts is accelerated by (1) heat, (2) pressure (including percussion), (3) shaking (no doubt by bringing fresh surfaces into contact).

3. The solubility and volatility of the salts greatly influence the reaction-velocity.

4. In the complete absence of water or other ionising solvent (*i.e.*, a solvent which becomes a conductor of electricity owing to the presence of the salt), *no reaction takes place.*

It would appear from these results that reaction between solid salts is of essentially the same nature as that between salts in solution. The quantity of water required to bring about a reaction is extremely minute, but its action is probably to ionise the salts. I would suggest that the water present forms a film on the surface of the salts, *and* that in this film minute quantities of the salts dissolve and there react. On this assumption, heat would accelerate reaction by increasing the solubility of the salts, and *also* by increasing their volatility if they had an appreciable vapour pressure. Pressure would in general bring more salt into solution, but would act chiefly by bringing the surfaces of the solids into close contact. Volatility would assist the reaction by carrying the particles of the volatile salt into contact with the surface of the other salt.

In the latter part of this work I have received most valuable assistance from Mr. J. H. Davies, B.Sc., to whom I here wish to express my indebtedness. I wish also to thank Professor A. C. Elliott for the use of the testing machine in the engineering department of this college.

Mercurammonium Base.—H. Gaudechon.—The author has shown that the mercurammonium base, $(NHg_2)_2O.nH_2O$, is formed instantaneously when mercuric oxide acts on dissolved ammonia. Five hydrates have been described, but only the monohydrate, $(NHg_2)_2O + H_2O$, is stable at the ordinary temperature in dry air. The hydrate with four molecules of water is stable in an atmosphere saturated with water vapour at 15°, and that with five molecules of water can exist only in presence of liquid water. Water at 100° decomposes the base into mercuric oxide and ammonia, $(NHg_2)_2O + 3H_2O = 2NH_3 + 4HgO$, and the brown oxide thus separated differs in crystalline form from the yellow and red varieties already known.—*Comptes Rendus*, cxliv., No. 23.

A METHOD FOR THE QUALITATIVE SEPARATION AND DETECTION OF FERROCYANIDES, FERRICYANIDES, AND SULPHOCYANIDES.

By PHILIP E. BROWNING and HOWARD E. PALMER.

THE ordinary method for the detection of ferrocyanides, ferricyanides, and sulphocyanides by means of ferric and ferrous salts leaves little to be desired in point of delicacy when these substances are not present together. When mixtures are to be examined, however, the colours tend to mask one another, and various methods to obviate the difficulty have been suggested, such as the bleaching of the red ferric sulphocyanide by mercuric chloride in testing for ferrocyanide, and the distillation of sulphocyanic acid before testing for that acid. In testing for a ferrocyanide in the presence of a ferricyanide the formation of the deep blue colour with the ferric salt or ferrous salt has generally been considered of sufficient delicacy for all practical purposes.

The work to be described is the result of an attempt to effect a separation of these substances one from another as well as to accomplish their detection.

Potassium ferrocyanide has long been mentioned as a precipitant of the ferrocyanides of the rare earth elements, cerium, thorium, yttrium, zirconium, &c., while it is also known that ferricyanides of these elements are soluble. These facts suggested the use of a member of the above mentioned group as a precipitant of the ferrocyanogen ion, and selection was made of a soluble salt of thorium as perhaps the most satisfactory and available.

A solution of potassium ferrocyanide was made by dissolving 1 grm. of the salt in a litre of water, and measured portions of this solution were used when amounts of 5 mgrms. or less were required. This solution was neutral to litmus and remained so throughout the investigation, as shown by frequent tests.

The delicacy of the reaction was tested by adding to portions of the solution enough water to make the total volume between 5 cc. and 10 cc., acidifying faintly with acetic acid or hydrochloric acid and adding a few drops of a 10 per cent solution of thorium nitrate. Amounts of the ferrocyanide as small as 0·0001 grm. gave a distinct cloudiness to the solution. Similar experiments made in the presence of 0·1 grm. of potassium ferrocyanide and 0·1 grm. of potassium sulphocyanide showed that these salts did not interfere with the delicacy of the test. In order to test the effect of dilution and the highest delicacy of the reaction, some precipitations were made in 100 cc. and 500 cc. of water, and it was found possible to detect 0·0005 grm. in 100 cc. of water and 0·0010 grm. in 500 cc. of water, or one part of the ferrocyanide in 500,000 parts of water.

The presence of considerable amounts of alkali acetates have a tendency to decompose the thorium ferrocyanide into soluble products, but this tendency may be overcome by further addition of thorium salt or hydrochloric acid.

Some difficulty was found in filtering the thorium ferrocyanide on paper alone, on account of its finely divided condition, but this difficulty was removed by agitating the liquid and suspended precipitate with some finely shredded asbestos before filtration.

In making the choice of a precipitant for the ferricyanogen ion with a view to subsequent testing for the sulphocyanogen ion by the ferric salt, some reagent giving a colourless solution was preferable. Salts of the elements zinc and cadmium meet this condition, and cadmium salts proved to be the more delicate. Following the general method already mentioned, it was found that 0·0001 grm. of the ferricyanide could be readily detected in from 5 cc. to 10 cc. of water acidified with acetic acid even when 0·1 grm of potassium sulphocyanide was present. The cadmium ferricyanide presented the same difficulty in filtration that has been described in the case of the thorium ferrocyanide, and the difficulty was overcome in the same manner.

The method as recommended is as follows:—The solution to be tested, preferably dilute and about 5 cc. to 10 cc. in volume, is acidified faintly with acetic acid or hydrochloric acid and treated with a soluble thorium salt to complete precipitation. To the liquid and suspended thorium ferrocyanide some finely shredded asbestos is added, the whole is agitated and thrown on a filter, and the precipitate washed with a little water.

The presence of the ferrocyanide may be confirmed by decomposing the washed precipitate with strong sodium hydroxide on the filter, acidifying the clear filtrate with hydrochloric acid, and testing with ferric chloride.

The filtrate from the thorium ferrocyanide is treated with a soluble cadmium salt to complete precipitation of the cadmium ferricyanide, which after the addition of the asbestos is filtered and washed as previously described. The presence of the ferricyanide may be confirmed by treating the cadmium ferricyanide with sodium or potassium hydroxide, acidifying the filtered solution, and testing with a ferrous salt.

The filtrate from the cadmium ferricyanide is acidified with hydrochloric acid and treated with ferric chloride, which gives the red ferric sulphocyanide.

The method is especially recommended for the detection of small amounts of ferrocyanides and ferricyanides in the presence of each other. The following table gives some results obtained:—

$K_4FeC_6N_6$ present. Grm.	$K_3FeC_6N_6$ present. Grm.	KSCN present. Grm.	Indication.
	Tests for $K_4FeC_6N_6$ *only*.		
0·0010	0·1	0·1	Distinct.
0·0005	0·1	0·1	
0·0002	0·1	0·1	
0·0001	0·1	0·1	
	Tests for $K_3FeC_6N_6$ *only*. (These tests were made without waiting to wash the ferrocyanide precipitate thoroughly).		
0·1	0·0010	0·1	Distinct.
0·1	0·0005	0·1	Fairly distinct.
0·1	0·0002	0·1	Faint.
0·1	0·0001	0·1	Very faint.
	Tests for KSCN *only*.		
0·1	0·1	0·0010	Distinct.
0·1	0·1	0·0005	
0·1	0·1	0·0002	
0·1	0·1	0·0001	
	Tests for $K_4FeC_6N_6$, $K_3FeC_6N_6$, *and* KSCN.		
0·0100	0·0100	0·0100	Good tests for $K_4FeC_6N_6$, $K_3FeC_6N_6$, and KSCN.
0·0050	0·0050	0·0050	
0·0010	0·0010	0·0010	
	Tests of Mixtures Unknown to Analyst.		
0·0010	0·0010	—	Found: $K_4FeC_6N_6$ and $K_3FeC_6N_6$.
0·0010	—	0·0010	Found: $K_4FeC_6N_6$ and KSCN.
0·0010	0·0010	0·0010	Found: $K_4FeC_6N_6$, $K_3FeC_6N_6$, and KSCN.

—*American Journal of Science*, [4], xxiii., No. 138.

His Majesty the King of Greece has conferred upon Mr. Geo. G. Blackwell the Gold Cross of Officer of the Royal Order of The Saviour, this decoration being made in recognition of his services in connection with the development of the mining industries of Greece. Mr. Geo. G. Blackwell is chairman of the firm of Geo. G. Blackwell, Sons, and Co., Ltd., of Liverpool and London.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 20th, 1907.

Sir WILLIAM RAMSAY, K.C.B., F.R.S., President, in the Chair.

CERTIFICATES were read for the first time in favour of Messrs. Arthur John Banks, 61, Lawton Road, Waterloo, Liverpool; John Kaye, M.A., B.Sc., Westerfield, Perth; Marcus Wechsler, D.Sc., 136, Sinclair Road, Kensington, W.

Certificates have been authorised by the Council under By-Law I. (par. 3) in favour of Messrs. David Leo Behrmann, 75, Sivewright Avenue, Doomfontein, Transvaal; William Bush Schober, B.Sc., Ph.D., Lehigh Univ., South Bethlehem, U.S.A.

A Ballot for the Election of Fellows was held, and the following were subsequently declared duly elected:—William Arthur Colebourn; Hugh Hague Copping, B.A.; Matthewman Dalton Cowap; Owen Aubrey Elias; Eugen Fischer, Ph.D.; Walter George Gledhill, M.A.; John Atkinson Jennings; Charles William Lamb Jensen; Percival George Lloyd; Walter Harold Nuttall; Harold Pochin, B.A.; Ruchi Ram Sahni, M.A.; Charles Kenneth Tinkler, B.Sc.; Charles Horne Warner; Walter Ormston Young; Israel Hyman Zortman, B.Sc.

Of the following papers those marked * were read:—

* 134. "*Some Properties of Radium Emanation.*" By ALEXANDER THOMAS CAMERON and Sir WILLIAM RAMSAY, K.C.B.

It has been discovered that the emanation from radium undergoes a rapid change of volume shortly after its change from the solid to the gaseous state; this is followed by a slow change, corresponding with its loss of electrical activity. Glass tubes, as well as silica tubes, were used for the experiments. The absorption of helium, hydrogen, oxygen, and carbon dioxide was investigated in these tubes so as to estimate the necessary corrections for the loss of volume by the emanation. It has been shown by thirty sets of measurements that the emanation behaves in accordance with Boyle's law, both before and after this preliminary change. Measurements have been made of the initial volume of the emanation, obtained from a solution of 87·7 mgrms. of radium (metal) as bromide and sulphate. From these it would appear that, instead of the previously accepted value for the average-life-period of radium, 1100 years, a much shorter life must be deduced, namely, 236 years. The change of fresh emanation is accompanied by a halving of its volume, and reasons were adduced for the belief that this change corresponds with its polymerisation from Em^1 into Em^2; the change, as shown by time measurements, is a unimolecular reaction, and the subsequent rate of contraction agrees numerically with the loss of electrical activity. It has also been shown that helium, contained in silica vessels, may pass into the walls, but the conditions under which this absorption takes place have not been elucidated. Lastly, a deposit consisting doubtless of radium D has been observed; it is a brown substance, with a submetallic lustre, not easily attacked by oxygen. The half-life-period of radium D is said to be forty years, whilst those of radium A, B, and C are only a few hours.

DISCUSSION.

Professor CLOWES asked whether statements made by Dr. Thorpe that afternoon, which were supplementary to his Bakerian lecture, might not explain the presence of free hydrogen after exploding the mixture of oxygen and hydrogen arising from the decomposition of water. The lecturer had mentioned that he had invariably noticed an odour of ozone and of hypochlorite from solutions of radium bromide. If ozone were formed, this would lead to removal of oxygen by the action of the mercury in the pump, and if hypochlorite were produced, oxygen would remain combined in the solution. An excess of hydrogen would in either case remain after the explosion.

Mr. BALY asked whether it were not possible that the discrepancy between Sir William Ramsay's and Prof. Rutherford's values for the life of the radium atom could be explained by the life being shortened in the presence of the emanation. It was necessary to assume that the radium atom was in a very unstable condition, and it appeared possible that its disintegration might be assisted by the bombardment due to the decomposition of the emanation. Prof. Rutherford made his observations with a very thin layer of radium bromide on a plate from which the emanation readily escaped. Sir William Ramsay on the other hand allowed the solution of radium bromide to stand for periods of four days during which time the emanation was concentrating in the solution.

In reply to a question from Prof. Rutherford, Sir W. RAMSAY stated that the emanation, when it passes from the solid to the gaseous state, passes at once into a monatomic gas, although one would imagine that a diatomic gas would be preferably formed. This may conceivably be connected with another unusual phenomenon which it displays; for at 80° the diatomic gas reverts almost entirely to its monatomic state, at 132° the reversion is not so complete, and at 237° still less complete. This is contrary to the general behaviour of compounds, yet it is not inconceivable that a higher temperature might prove favourable to combination and that a diatomic gas may be more stable at high than at low temperatures. The author, however, maintained that he was there to chronicle and not to defend the behaviour of the emanation.

The volume of helium produced from 1 volume of an emanation is about 3½ volumes—agreeing in this respect with Prof. Rutherford's contention that the α-particle is a helium atom. In reply to Prof. Clowes, it was pointed out that no ozone is produced from a solution of radium bromide although the solid bromide has an odour of ozone.

*135. "*The Affinity Constants of Aminosulphonic Acids as Determined by the Aid of Methyl-orange.*" By VICTOR HERBERT VELEY.

In continuation of a former investigation on this subject (*Trans.*, 1907, xci., 153) the affinity constants of certain aminonaphtholsulphonic acids have been determined, and the general results are as follows:—

1. The affinity constants of the aminonaphtholsulphonic acids when determined by the tintometer method show, as regards the effect of the introduction of the hydroxyl grouping in the naphthylaminesulphonic acids, relationships similar to those observed by Ostwald by the electric conductivity method for the hydroxybenzoic acids as compared with benzoic acid.

2. One possible case of steric hindrance induced by the introduction of the hydroxyl grouping in the 8-position was noted.

Attempts were made to examine the naphtholsulphonic acids by the above method, but the acidic reaction appeared to be mollified by some subsequent secondary change.

*136. "*Aso-Derivatives of* 1 : 3-*Diphenylbarbituric Acid. Dynamic Isomerism among the Coloured Hydrazones of* 1 : 3-*Diphenylalloxan.*" By MARTHA ANNIE WHITELEY.

In order to throw some light on the structure of the compounds obtained by the action of aromatic diazonium chlorides on the 5-alkyl-substituted derivatives of 1 : 3-diphenylbarbituric acid (*Proc.*, 1906, xxii., 201), the investigation has been extended, and the action of the β-substituted derivatives of phenylhydrazine on 5 : 5-dibromo-1 : 3-diphenylbarbituric acid has been examined. The results show that the compounds obtained in the first reaction are *aso*-derivatives, whilst those obtained in the second are *hydrazones*.

In the course of the investigation the following com-

pounds have been prepared :—5-*Benzeneazo*-5-*benzyl*-1 : 3-*diphenylbarbituric acid*,—

$$CO<^{NPh\cdot CO}_{NPh\cdot CO}>C<^{CH_2Ph}_{N:NPh};$$

5-*benzeneazo*-5-*diphenylmethyl*-1 : 3-*diphenylbarbituric acid*,—

$$CO<^{NPh\cdot CO}_{NPh\cdot CO}>C<^{CHPh_2}_{N:NPh};$$

the *nitro*-derivative,—

$$CO<^{NPh\cdot CO}_{NPh\cdot CO}>C<^{CHPh_2}_{N:N\cdot C_6H_4\cdot NO_2}$$

melt and decompose at 170—171°, 160°, and 175° respectively. These compounds are yellow. 1 : 3-*Diphenylalloxanphenylmethylhydrazone*,—

$$CO<^{NPh\cdot CO}_{NPh\cdot CO}>C:N\cdot NPhMe;$$

1 : 3-*diphenylalloxandiphenylhydrazone*,—

$$CO<^{NPh\cdot CO}_{NPh\cdot CO}>C:N\cdot NPh_2;$$

1 : 3-*diphenylalloxanphenylbenzylhydrazone*,—

$$CO<^{NPh\cdot CO}_{NPh\cdot CO}>C:N\cdot NPh(CH_2Ph),$$

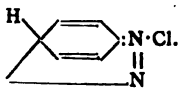
melt and decompose at 175°, 254—255°, and 130—131° respectively; these compounds exist in two forms, one yellow and one red.

*137. "*A Series of Coloured Diazo-salts derived from Benzoyl*-1 : 4-*Napthylenediamine*." By GILBERT THOMAS MORGAN and WILLIAM ORD WOOTTON.

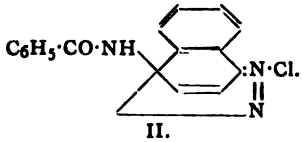
The examination of the diazo-salts of benzoyl-*p*-phenylenediamine and benzoyl-1 : 4-naphthylenediamine has been continued and it has been found that the diazo-derivatives of the latter base are extremely stable substances which are invariably coloured.

Benzoyl-4-*aminonaphthalene*-1-*diazonium chloride*, $C_6H_5\cdot CO\cdot NH\cdot C_{10}H_6\cdot N_2\cdot Cl$, m. p. 140° with decomposition, crystallises in well-defined yellow needles which retain their colour after repeated crystallisation from water or fractional precipitation from different organic media. The corresponding *bromide*, *iodide*, *sulphate*, *nitrate*, *nitrite*, *chlorate*, *perchlorate*, *carbonate*, *trichloracetate*, and *thiocyanate* have been prepared. The sulphate crystallises in golden-yellow leaflets or needles, whilst the perchlorate, which is quite stable in the dry state, separates in sparingly soluble, light yellow crystals, and is the palest compound of the series. These compounds have the chemical properties of diazonium salts, and couple readily with alkaline β-naphthol to furnish azo-derivatives. With potassium cyanide they yield *benzoyl*-4-*aminonaphthalene*-1-*diazocyanide*, a stable red microcrystalline compound which does not couple with alkaline β-naphthol.

These coloured salts might be regarded either as *syn*-diazo-derivatives or as equilibrium mixtures of diazonium and *syn*-diazo-derivatives, although their great stability somewhat militates against the assumption that they consist wholly or in part of *syn*-diazo-compounds. The existence of such a series of coloured diazo-salts would be anticipated from the formulation recently suggested by Cain for diazonium salts (Formula I.).



I.

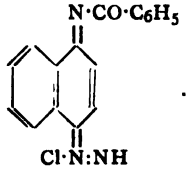


II.

According to this view, the appearance of colour in the foregoing series may be connected with the replacement of a benzene by a naphthalene nucleus and the substitution of the hydrogen atom of Formula I. by the heavy group $C_6H_5\cdot CO\cdot NH$ of Formula II.

DISCUSSION.

Dr. HEWITT thought it very probable that coloured diazonium salts might possess a quinonoid structure. But as in all cases when the salts were coloured they allowed of a true quinonoid formulation, Dr. Morgan's compound might well have the constitution—



whilst the constitution Dr. Morgan assigned to the salt more resembled that of the "chinols" of Bamberger, which are colourless.

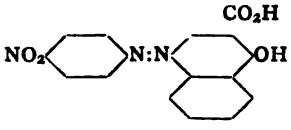
Dr. CAIN thought there was much danger in speculating as to the colour of a compound entirely from the quinonoid or non-quinonoid state of only a part of the molecule. The rest of the molecule, as Dr. Morgan had pointed out, was of much importance in attempting to arrive at an explanation of the colour.

In reply, Dr. MORGAN said that he preferred the formula for diazo-salts advocated by Dr. Cain to those which required the presence of a labile hydrogen atom in the para-position to the diazonium complex because the former configuration was applicable both to the simpler colourless diazonium salts and also to the more complex coloured diazo-derivatives described in this communication. The development of colour in this series of substances seemed to depend to some extent on the nature of the aromatic nucleus and partly on the presence of a complex substituent in the para-position to the diazo-nitrogen. Further experimental evidence, however, would be required before the conditions determining the appearance of colour among the diazonium derivatives could be completely defined.

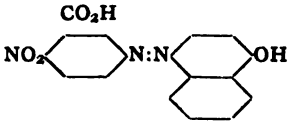
*138. "*Colour and Constitution of Azo-compounds*." (Part I.). By JOHN THEODORE HEWITT and HERBERT VICTOR MITCHELL.

The authors recently drew attention to the very marked change in colour when *p*-nitro-derivatives of arylazo-*p*-phenols were dissolved in alkalis (*Trans.*, 1896, lxxxix., 13, 17). The explanation was offered that whilst benzeneazophenol forms alkaline salts of corresponding constitution, the *p*-nitro-derivatives furnish salts with the metal attached to the nitro-group, and therefore diquinonoid in structure. The relationships are rendered apparent by the formulæ $C_6H_5\cdot N:N\cdot C_6H_4\cdot OK$ and $KO_2N:C_6H_4:N\cdot N:C_6H_4:O$.

Definite proof has been obtained of the correctness of this view by a comparison of the two carboxylic acids derived from *p*-nitrobenzene-azo-α-naphthol of the formulæ—



and—



Both these compounds give deep blue alkaline solutions, but, whilst the former yields brown precipitates with salts of heavy metals, the latter gives blue precipitates; no doubt in the latter case the lead salt has the constitution $O:C_{10}H_6:N\cdot N:C_6H_3<^{CO\cdot O}_{NO\cdot O}>Pb$.

The following compounds were described :—

2-*Nitro*-5-*acetylaminobenzoic acid*, m. p. 210—220° (with decomposition). 2-*Nitro*-5-*aminobenzoic acid*, m. p. about 235°. p-*Nitro*-m-*carboxybenzeneazo*-α-*naphthol*, m. p. 260°. o-*Nitrobenzeneazo*-α-*hydroxy*-3-*naphthoic acid*, m. p. 200°. m-*Nitrobenzeneazo*-α-*hydroxy*-β-*naphthoic acid*, m. p. 220—225°. p-*Nitrobenzeneazo*-α-*hydroxy*-β-*naphthoic acid*, m. p. 242°. p-*Nitro*-m-*carboxybenzeneazophenol*, m. p. 195°. p-*Nitro*-m-*carboxybenzeneazo*-o-*nitrophenol*, m. p. 213°. p-*Nitro*-o-o-*dibromophenol*, m. p. 205—206°. p-*Nitrobenzeneazosalicylaldehyde*, m. p. 192—193°; its *acetyl* derivative, m. p. 150°, and *phenylhydrazone*, m. p. 235—240°. The melting-points in this and the preceding papers are uncorrected, the decomposition which occurs rendering accurate observation impossible.

The general result arrived at is that the frequency of the absorbed light is lowered by increase in the length of the chain of alternate single and double linkings. The introduction of substituents may modify the length of the chain owing to the possibility of more stable salt formation in other directions.

(To be continued).

PHYSICAL SOCIETY.

Ordinary Meeting, June 14th, 1907.

Mr. H. M. Elder, Vice-President, in the Chair.

A paper by Mr. Upson, on the "*Electric Arc*," was read by the author.

It dealt with observations made during the past Session at the Pender Electrical Laboratory, at the suggestion and under the direction of Prof. Fleming, F.R.S., with the object of elucidating some of the facts connected with the production of electric arcs between cooled metal and carbon terminals, in air and hydrogen. Apparatus was exhibited for maintaining the arc in various gases, while one electrode was cooled by means of a water circulation. Arcs were described in which the electrodes consisted of carbon, copper, iron, and aluminium in different combinations, maintained in air, hydrogen, and coal-gas. With 110 volts supply, metal arcs in hydrogen took the form of a spark-discharge. At that voltage the maximum length of arc it was possible to obtain, with current up to 15 ampères, was 0·05", except where both electrodes were of the same metal. When carbon is one of the electrodes a true arc is formed. If carbon is negative the maximum length of arc with the above voltage is 0·07". Volt-ampère characteristic curves were shown for arcs in air and hydrogen of length 0·05". The general position of the curve is determined by the material of the negative electrode. With carbon negative, in hydrogen, the curves for various positive electrodes very nearly coincide. With carbon positive, they keep the same curvature, but vary in distance apart, according to the material of the negative. In general, the position of the curve is governed by the negative, but its particular shape seems to come from the influence of the surrounding gas. The slope of the curve (ampères horizontal, volts vertical) of the carbon arc in air, is much less steep than that of the curve of any arc in hydrogen. The former curve cuts the latter in the neighbourhood of 6·5 ampères. The curve for the arc with carbon positive, aluminium negative, in air, is very steep, being equal in this respect to the curves for arcs in hydrogen. Volt-ampère characteristics were shown for copper arcs in air, with (1) positive electrode cooled, (2) negative electrode cooled, and (3) neither cooled. Equations for various arcs were obtained giving the voltage in terms of current and arc-length. It was much more difficult to obtain a carbon arc in hydrogen with alternating currents; and no arc could be obtained when the electrodes were copper positive, and carbon negative, with 100 volts supply and frequencies of 50 and 80. Similar results were obtained in coal-gas. Apparatus was devised in accordance with a suggestion by Dr. Fleming, to interrupt the arc for a definite period of time. Experiments were tried to determine how long the arc could remain extinguished without losing the power of re-starting itself when the electromotive force was again applied. Curves were shown for arcs with electrodes of solid and cored carbons, in air. With cored carbons the time of interruption is greater than with solid, and both are much greater than that for the copper-carbon arc. In hydrogen the copper-carbon arc could not be made to re-start itself if the electro-motive force was removed for more than 0·04 of a second, and for this arc the minimum interruption possible is far shorter than for any carbon arc in air.

Mr. W. Duddell said the paper was a most interesting one. He asked if the author had noted the character of the different arcs which he had used. The characteristic curves for arcs in coal-gas or hydrogen were steeper than those in air, and therefore arcs in coal-gas were more suitable for the production of oscillations. He asked if the curves remained steep when the current was quickly changed. He had noticed the phenomenon of an arc between two cored carbons re-lighting, and said that on high-voltage circuits the length of time was considerable, and amounted in some cases to seconds.

Mrs. Ayrton said the paper was a valuable one, but she was sorry the author had not given a careful description of the appearance of the arcs and carbons under different conditions, and also the observations upon which the curves were founded. It was difficult to arrive at any general conclusions from the author's curves. The steep parts depend not only on the composition of the electrodes but on their size and on the length of the arc. The author had only used short arcs which with carbons only gave the flat part of the curve. With metal-carbon you get the steep part. Mrs. Ayrton also expressed her interest in the re-lighting experiments shown by the author.

Mr. A. Campbell asked if the characteristic curve of a mercury arc was similar to that of the other metal arcs investigated. He pointed out that the use of unscientific units (inches and feet) in giving the results of such interesting researches was most deplorable. In all standard work on the subject the lengths of arc are always given in millimetres, and even in commerce the diameters of carbons are similarly expressed (*e.g.*, 12 mm. and not 0·47 inches).

Mr. Alexander Russell stated that Mr. Upson's paper would be extremely useful to all engaged in research in connection with the electric arc. He agreed with the author that coal-gas was very unsuitable for experiments with the arc. He had recently been experimenting with high-voltage alternating arcs in coal-gas, and in most cases the enclosing vessel was soon filled with black cobwebs. When, however, the high-voltage high-frequency arc between iron-iron electrodes was shunted by a Leyden jar in series with a small coil of wire the discharge between the electrodes became simply a torrent of sparks, and no appreciable quantity of soot was formed. The difficulty the author experienced in certain cases in obtaining an arc was due probably to the low voltages used. When high voltages are applied it is easy enough to maintain an arc. More experimental research was wanted on the upper part of the statical characteristic curve of the arc. A good deal of exploration has already been made in this direction in Dr. Simon's Laboratory at Göttingen with the help of a motor generator from which three or four ampères of direct current can be obtained at 5000 volts. The results already obtained were of great importance. The success of the statical characteristic method as an instrument of research was mainly due to the care with which Mrs. Aryton had specified the method of obtaining the curve. He hoped that Mr. Upson would make further researches at high voltages.

Dr. Fleming congratulated Mr. Upson on his paper, and said that it represented a considerable amount of careful work, and even if all the conclusions to be drawn from it were not yet absolutely clear, it would furnish a statement of facts which would assist in future theorising. He said

that the interesting part to him at the moment was the difference between the form of the volt-ampère characteristics for the carbon-carbon arc in air and the metal-carbon arc in hydrogen, but on that matter he would defer his remarks until he had shown some other experiments.

Mr. Upson, in reply, stated that the primary object of the paper was to compare metal arcs with carbon arcs. He had also performed some experiments with charge of voltage and variations in the length of burning of the arc, and he hoped to carry out a series of experiments using high voltages.

Experiments were then exhibited by Dr. J. A. Fleming, F.R.S., with the Poulsen Arc as a means of obtaining continuous electrical oscillations, repeating some of those shown by him at the Royal Institution on May 24th last.

Dr. Fleming showed and described an apparatus for forming an electric arc in an atmosphere of coal-gas between a carbon rod kept in slow rotation and a cooled copper anode, the arc being formed in a magnetic field of 600 to 1000 C.G.S. units. The arc was supplied with continuous current at a pressure of 400—500 volts. A condenser of 0·003 mfd. capacity in series with an inductance of 200.000 cm. was shunted across the arc, and experiments shown to prove the existence of high frequency oscillations in the condenser circuit. A long resonance helix of insulated wire was then joined to the condenser circuit, and when tuned to it created a powerful high frequency field round it in which vacuum tubes glowed brilliantly. By vibrating or rotating a Neon vacuum-tube of spectrum type near the helix, and showing that the band or disk of light was cut up by dark spaces, Dr. Fleming supported the contention that the oscillations so produced are not absolutely uninterrupted but cut up into groups. Another experiment was shown to confirm this. The oscillations produced by the arc in one circuit were caused to create secondary oscillations in another circuit in which was a condenser shunted by one of Dr. Fleming's oscillation valves and a telephone. The valve rectifies the secondary oscillations, and if they were absolutely continuous the telephone would be traversed by an uninterrupted direct current. But as a fact a discontinuous sound is heard in the telephone which can arise if the primary oscillations come in batches or groups.

Dr. Fleming then gave some figures showing the kind of values obtained for the efficiency of transformation of continuous to oscillatory current by the arc, and compared them with similar measurements for the spark method. He concluded with some discussion of the *modus operandi* of the metal-carbon arc in the production of oscillations in a shunt circuit containing capacity and inductance. In the first case the curve was (as shown from Mr. Upson's diagrams) much steeper than in the second. This implied that the same amount of energy could be conveyed to the oscillatory circuit by means of a condenser of smaller capacity, and therefore give higher frequency. This was confirmed by the fact that the curve for small currents in the case of the carbon arc in air was steeper than for large currents, and it was found that a Duddell carbon arc could give high frequency oscillations when actuated with small currents. He thought that there was still much work to be done before the whole of the phenomena of the oscillatory arc were understood.

Mr. W. Duddell expressed his interest in the experiments, especially those in which it was shown that the oscillations were broken up into groups. He pointed out, however, that it was possible to obtain continuous oscillations with a musical arc using high frequencies. The question as to the measurement of the power put into the Poulsen arc was of great interest, as also was the question as to the amount of power which could be taken from the secondary without stopping the arc. He questioned Dr. Fleming's statement that the power put into the arc was equal to the product "AV," and said that the power should be measured with a wattmeter.

Mr. A. Campbell remarked that Mr. Altberg in Odessa, had lately shown that sparks of high oscillation frequency produce actual air vibrations of the same frequency, and by measuring the wave lengths of these air vibrations by diffraction methods he had been able to determine the high frequency.

Dr. Fleming, in reply, said he was prepared to accept Mr. Duddell's criticism that the power put into the Poulsen arc should be measured with the wattmeter. The really important matter, however, was the reason why the metal-carbon arc in coal-gas could produce oscillations of so much higher frequency than the carbon arc in air. This he thought was intimately connected with the slope of the characteristic curve.

Mr. Rollo Appleyard exhibited a Direct-reading Conductivity Bridge for testing rods of steel or other material, where there is considerable range of conductivity between successive specimens, and where it is necessary to eliminate the resistance of end contacts.

The instrument is provided with two scales and with corresponding sliders. By setting one of the sliders with reference to its scale, compensation is made for any small difference of diameter or of mass between the standard rod and a test rod. The second slider is then adjusted to the position of balance, and the conductivity is read off the second scale as a percentage, according to Matthiessen's standard, or in terms of any desired unit. All arithmetic is avoided, and the results are obtained at the rate of two or three a minute. Mr. Appleyard gave the equations for the calibration of the scales, and showed that the errors involved by the use of the compensation scales were for practical purposes negligible.

Mr. A. Campbell said he had used the author's conductometer and testified to its convenience. He objected, however, to the measurement of conductivity in terms of Matthiessen's standard, and suggested that for work with nickel steels, &c., the bridge should be graduated in resistivities.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxliv., No. 23, June 10, 1907.

Oxidising and Decolorising Properties of Graphite.—Henri Louis Dejust.—To measure the decolorising power of graphite the author shook 1 grm. of it with 42 cc. of a solution of litmus containing 9·8 grms. of extract per litre at 100°. After shaking for thirty seconds it was filtered, and the colours of the filtrates compared with one another. The same graphite after purification (reducing its carbon to 93·1 per cent) produced less decoloration. If the medium in which the operation takes place is acid, neutral, or basic the effect is unaltered. With animal black, however, in a neutral or acid solution the decoloration is total, while in a basic solution it is less than when purified graphite is used. Graphite has an oxidising action like that of animal black. A solution of paraphenylene diamine left in air in contact with graphite in the cold turns brown, and this effect is accelerated by heating. It also decolorises a solution of litmus in absence of air; for example, when a flask of the solution which has been boiled is completely filled.

Nickel Acetate as a New Type of Oxidiser for Hydroquinone.—André Job.—Neutral acetate of cobalt brings about the oxidation of hydroquinone, but its activity soon diminishes and finally disappears. It is, however, easy to prepare an active nickel acetate which readily effects the oxidation of hydroquinone, surpassing even manganese acetate in this respect. It is prepared by

heating chemically pure nickel acetate for some time to 100°, when it loses acetic acid, but remains entirely soluble in water. The activity of both manganese and nickel acetate can be diminished by diminishing the amount present and also by adding acetic acid. With manganese if the activity is reduced by dilution, it is also rendered less lasting, while when acid is added the activity becomes more stable and remains constant from the commencement of the action. With nickel, on the other hand, a rapid diminution of the velocity of the action is caused, whichever way the activity is reduced. This is because heated nickel acetate has already lost acetic acid and owes its activity only to the free hydrate. The neutral manganese acetate is made active by the small amount of hydrate which its hydrolysis furnishes. The feeble acidity of the hydroquinone is sufficient to stop this hydrolysis, and the effect is more appreciable the smaller the amount of manganese present, but if the hydrolysis has already been checked by the addition of free acetic acid the effect of the hydroquinone is negligible. In the case of nickel, the addition of acetic acid only neutralises a little hydrate. Thus, nickel acetate modified by heat constitutes a new type of oxydase for hydroquinone, in which the influence of the metallic hydrate can be isolated and measured, by comparing the activity of the neutral acetate of nickel with that of modified acetate in which the amount of free hydrate is known.

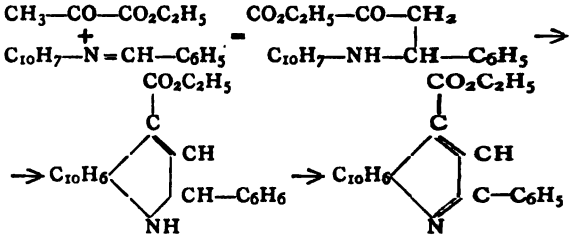
Compounds of Hypovanadic Acid with some Oxygenated Acids.—Gustave Gain.—Hydrated hypovanadic acid, $V_2O_4.2H_2O$, dissolves in a dilute solution of selenic acid, giving a blue crystalline powder, $V_2O_4.3{\cdot}5SeO_3.7H_2O$. When excess of selenic acid is used a selenate is deposited, but with much more difficulty. It has the composition $V_2O_4.5SeO_3.10H_2O$. The corresponding sulphates differ from these only in the number of molecules of water, being $V_2O_4.3{\cdot}5SO_3.10H_2O$ and $V_2O_4.5SO_3.12H_2O$. When phosphoric acid is substituted for selenic acid the compounds formed are $V_2O_4.2P_2O_5.6H_2O$ and $V_2O_4.3P_2O_5.10H_2O$, and with arsenic acid the product is $V_2O_4.3As_2O_5.6H_2O$.

Relations between the Diagram of Binary Alloys and their Malleability.—Léon Guillet.—I. When the metals are deposited in a pure state, if they are both malleable, so are all the alloys; if neither metal is malleable, no malleable alloy can be prepared; and if one metal is malleable and the other is not, the malleability of the alloys depends upon that of the eutectic. II. When the metals are only miscible in the solid state in the neighbourhood of the pure metals, and do not form combinations, if one of the metals is malleable, the solid solution rich in this metal is always malleable. III. When the metals form combinations or solid solutions which solidify at a constant temperature, only those alloys which are at the extremities of the diagram are malleable. IV. When the alloys form solid solutions which decompose before liquefying, an alloy formed of a pure malleable metal, or of a solid solution very rich in this metal and a compound, will possess only feeble malleability. An alloy formed of two solid solutions, one of them rich in malleable metal, is only malleable if the proportions of the second are low. V. When the metals are miscible in all proportions, if one metal is malleable, so are all the alloys; the only exception to this rule is the iron-manganese alloy, but the manganese employed is very impure.

Mechanism of the Synthesis of Quinoline Derivatives.—L. J. Simon and Ch. Mauguin.—When pyruvic acid, CH_3COCO_2H, acts in alcoholic solution on a primary aromatic base in presence of an aldehyde a phenylquinolinic acid is obtained:—

$$C_{10}H_7NH_2 + CH_3COCO_2H + C_6H_5COH = \\ = 2H + H_2O + C_{20}H_{10}O_2N$$

(Döbner). The authors have investigated the mechanism of this reaction, using chloroform or benzene as solvent and substituting benzylidene β-naphthylamine for the β-naphthylamine. They have thus obtained the following products:—(1) Methylnaphthoquinoline carboxylic acid; (2) phenylnaphthoquinoline carboxylic acid; (3) tetrahydrophenylnaphthoquinoline carboxylic acid; (4) benzylnaphthylamine. Apparently an intermediate product is formed and the transformations can be represented by the equations:—

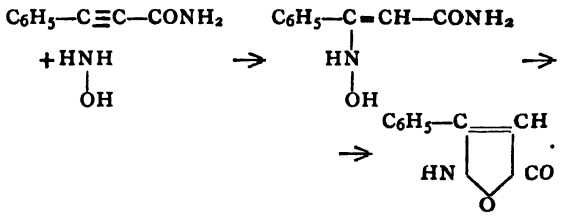


Ether Function of Diphenol.—R. Delange.—The group $\begin{matrix}-O\\-O\end{matrix}\!>\!CCl_2$ is easily transformed into $\begin{matrix}-O\\-O\end{matrix}\!>\!CO$ by the action of cold water. When cold water acts on tetrachloride of piperonal a new compound is obtained which, when boiled with water or dilute acids, undergoes the following reaction:—

$$CO\!<\!\begin{matrix}O\\O\end{matrix}\!>\!C_6H_3{-}CHCl_2 + 2H_2O = \\ = \begin{matrix}OH\\OH\end{matrix}\!>\!C_6H_3{-}CHO + CO_2 + 2HCl.$$

Caustic potash acts violently upon the dichloromethylenic compounds, giving a substance in which the molecule is doubled and the chlorine eliminated, $\begin{matrix}-O\\-O\end{matrix}\!>\!C = C\!<\!\begin{matrix}O-\\O-\end{matrix}$.

Action of Hydroxylamine upon Nitriles, Acetylenic Amides, and Ethereal Salts, and on the corresponding β-Ketonic Compounds.—Ch. Moureu and I. Lazennec.—When a methylic solution of hydroxylamine, separated from its chlorhydrate by sodium methylate, acts on phenylpropiolic nitrile a compound, $C_9H_8N_2O$, is formed. When this is boiled with concentrated hydrochloric acid it yields $C_9H_7NO_2$. This appears to be formed as follows:—



The substance $C_9H_8N_2O$ is 3-phenyl-5-iso-azolonimine. Unsubstituted β-ketonic nitriles give the same products of condensation with hydroxylamine, viz., cyclic compounds containing two atoms of nitrogen. Acetylenic amides and ethereal salts give the same compounds as are obtained with the corresponding amides and β-ketonic ethereal salts. These derivatives are isoxazolones.

MISCELLANEOUS.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 1st inst., Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. Mr. G. Jamieson, C.M.G., Dr. S. Shore Nightingale, Mr. W. Stone, Mr. H. S. Stoneham, and Mr. E. Turk were elected Members.

ERRATUM.—Vol. xcv., p. 301, col. 1, line 31 from bottom, *for* "6L₈" *read* "*b*L₈."

A NEW VOLUME OF THE "TEXT-BOOKS OF PHYSICAL CHEMISTRY" IS NOW READY.

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STEREOCHEMISTRY.

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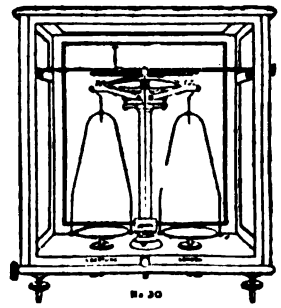

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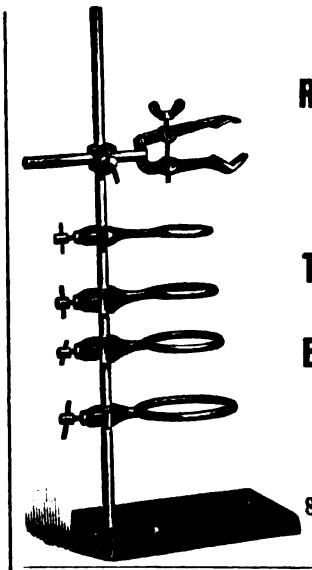

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RADIO-ACTIVE LEAD AND GRIGNARD'S REACTION.

By K. A. HOFMANN and V. WÖLFL.

RADIO-ACTIVE lead has recently been made the subject of exhaustive physical investigations. In agreement with the qualitative results obtained by Hofmann (*Ann. d. Physik*, 1904, [4], xv., 615), Gonder and Wölfl, Stefan Meyer (*Wiener Sitzungsberichte*, July, 1905, cxiv., ii.*a*, and *Jahrb. der Radio-aktivität und Electronik*, 1906, iii., 385), and Egon v. Schweidler proved by quantitative measurements that there is present in radio-lead a substance which does not emit rays, but suffers a transformation (Period of decay of activity to the half value = about 40 years). This is called RaD from its position in the decay series, and from it is developed directly a β-radiating substance RaE_2, with the half-constant of 4·8 days; this in turn passes into RaF, which emits only α-rays, and has a period of decay to the half value = 137 days.

In this series, RaD no radiation $\rightarrow$ RaE_1 no radiation $\rightarrow$ RaE_2 β-radiation $\rightarrow$ RaF α-radiation, is contained the group of the uranium derivatives belonging to the heavy metals, and it forms the end of the radio-active decay of uranium according to Rutherford's hypothesis (*Phil. Mag.*, 1904, viii., 636; *Nature*, 1905, lxxi., 341).

Rutherford, Soddy, and Boltwood assume that the final stable product is ordinary inactive lead, which Hofmann and Strauss (*Berichte*, 1900, xxxiii., 3126), had already detected in uranium minerals, and the amount of which was proved by Boltwood (*Amer. Journ. Science, Silliman*, [4], xxiii., 77), to be proportional to the amount of uranium present in unchanged primary minerals. But when we reflect that, as the decay of the members of the above series proceeds, they become electrochemically more positive (St. Meyer and E. von Schweidler, *Jahrbuch der Radioaktivität und Electronik*, 1906, iii., 395), we shall also include among the products of final decay tellurium (W. Marckwald, *Berichte*, 1902, xxxv., 4239), which is very closely allied to RaF, and the substance similar to platinum which I discovered in the lead of pitchblende, and the spectrum of which shows at least two unknown lines, $\lambda = 4995$ and $\lambda = 2785$.

The aim of our experiments was now to examine as fully as possible the analytical characteristics of RaD compared with those of RaF, in order thus to isolate the separate members.

RaF, radio-tellurium, is, according to Marckwald (*Berichte*, 1902, xxxv., 4239), separated as an electro-positive substance from a hydrochloric acid solution of bismuth-polonium by means of copper or bismuth. We were convinced that no other substance with a more lasting activity could be isolated from such solutions, for precipitates with equal decay constants were formed on electrochemically different metals.

According to the formula $I = I_0 e^{-\lambda t}$, λ for lead-foil is 0·00521, for silver-foil 0·00515, for lead-foil 0·00516, for platinum foil 0·00516. Hence the calculated value for the time required for the half decay is 134·4 days. Marckwald (*Jahrbuch der Radioaktivität und Elektronik*, 1905, ii., 136), found for radio-tellurium 139·6 days; according to Stefan Meyer (*Wiener Sitzungsberichte*, 1906, cxv., ii.*a*, 63) and Egon v. Schweidler the time is 136·5 days.

Even in a solution of radio-lead chloride containing RaD with RaF, only RaF can be detected as a more lasting principle giving α-rays.

We found for λ from the decay equation $I = I_0 e^{-\lambda t}$, for lead $\lambda = 0{\cdot}0051$, for copper $\lambda = 0{\cdot}0053$, for silver $\lambda = 0{\cdot}0051$; thus the mean value was $\lambda = 0{\cdot}00516$, which is the same as with bismuth-polonium solution.

RaF is chemically different from bismuth, for Marckwald (*Berichte*, 1902, xxxv., 4239), states that it is closely analogous to tellurium. We succeeded in obtaining from the mother-liquors of bismuth-free radio-lead chloride solution by means of an alcoholic mixture of hydrochloric and sulphuric acids, a substance which emitted much α-radiation; this substance agreed analytically with lead, even to the solubility of its sulphate; and according to Prof. Exner its spectrum showed only lead lines. The original strength was found by Egon v. Schweidler to be 3000 uranium units when the surface was the same; since 1·5 grms. of uranium corresponded to 0·005 grm. of the substance, the activity of a given weight must be considerably greater. For this preparation, which was undoubtedly free from bismuth, Stefan Meyer and E. v. Schweidler (*Wiener Sitzungsberichte*, 1906, cxv., ii.*a*, 63), found 134·5 days for the period of decay to the half value.

As RaF in bismuth-polonium follows bismuth as oxychloride and oxynitrate as the only α-active constituent, which has recently been proved by Sk. Curie (*Comptes Rendus*, cxlii., 273), it follows that RaF has analytically the mixed characteristics of bismuth, lead, and tellurium, if we do not prefer to assume that RaF is allied to these elements in the same way as a member of the sulphur group. In our opinion this is shown by the fact which we have already reported (*Ann. d. Physik*, 1904, iv., xv., 625), that even noble metals such as palladium, platinum, iridium, and rhodium, take up RaF readily from solutions, which cannot be interpreted to mean that these metals separate RaF electrochemically, for then it would have to be still more electro-positive than these last members of the potential series. Also when radio-lead acetate or nitrate is electrolysed, RaF is separated not only at the calthode (see also St. Meyer and E. v. Schweidler, "Lieben-Festschrift," 404, and Hofmann's earlier statement, *Ann. d. Physik*, 1904, xv., 621), but also at the anode in considerable quantities—in one operation up to as much as 300 uranium units; but this amphoteric behaviour may be caused by the formation of a higher oxide.

In electrolytic, electrochemical, and hydrolytic processes, RaF is followed by the β-radiating (F. Giesel, *Berichte*, 1906, xxxix., 780), but extremely rapidly decaying RaE_2, with the period of decay to the half value of 4·8 days. (H. v. Meyer and E. v. Schweidler, "Lieben-Festschrift," 408).

Our recent experiments were aimed chiefly at isolating RaD, the comparatively long existence of which (period of decay to the half value = 40 years), renders possible a more detailed chemical characterisation. Although the difficulties of separation from inactive lead are extraordinarily great, we discovered several ways of effecting it.

The partial crystallisation (Hofmann, *Ann. d. Phys.*, 1904, xv, 621), of the chloride from water, or better, from strong hydrochloric acid, leads to an accumulation of RaD in the first, difficultly soluble parts, while RaE and RaF pass into the mother-liquors.

The distillation of radio-active lead chloride in presence of some ammonium chloride is much quicker; RaD, as well as RaE and RaF, then volatilises more easily than ordinary lead chloride. If RaE and RaF are removed from the distillate by repeated crystallisation from strong hydrochloric acid, and the first crystals are purified by precipitation from aqueous solution with sulphuretted hydrogen, the sulphide is at first hardly active, but gradually develops α and β activity in a far higher degree than the original material. In the electrolysis of nitrate and acetate solutions the RaD goes to a slight extent to the anode, and is much concentrated at the cathode if this consists of mercury. A preparation as sulphate enclosed in a completely exhausted capillary after a period of several months showed distinctly the helium lines $\lambda = 587{\cdot}5$, $501{\cdot}6$, $447{\cdot}1$, while with RaE and RaF all our experiments in this direction

have so far given absolutely no result. (See also Grienacher, *Naturwissenschaftl. Rundschau*, 1906, xxi., 671; we shall return to this point elsewhere). No radium emanation could be detected in any preparation.

If zinc is allowed to act for some time on fused radio-lead chloride, RaD, RaE, and RaF accumulate in the metallic regulus (the two latter very strongly), while only RaE and RaF are reduced when it is fused with silver foil.

But all these methods lead ultimately to the formation of preparations in which the ratio of RaD to inactive lead cannot be altered to such an extent that the isolation of RaD seems possible.

Much better results are obtained by a method which we have worked out with G. Ebert, and which is of general chemical interest, namely, the conversion of lead chloride into lead tetraphenyl, using phenyl magnesium bromide.

Magnesium shavings are rendered active not with iodine, as usual, but with a few drops of bromine; then bromo-benzene in absolute ether is added, and after the phenyl magnesium bromide is formed it is mixed with lead chloride, powdered as finely as possible, made to a paste with benzene, and thoroughly dried. The mass soon becomes black, owing to the separation of metal, and after shaking for several hours the magnesium compound can no longer be used to form lead phenyl. The tetra- and not the di-phenyl compound is thus prepared, half of the lead separating as metal. After filtering the residue is washed with benzene, and all the filtrate evaporated to one-third, shaken up with water, and then again dried and filtered; the benzene solution is then evaporated to crystallisation. The di-phenyl must be removed from the mixture of crystals by ligroin or gasoline, and the residue of lead phenyl again re-crystallised from a little benzene. The crystals melt at 229° and consist of colourless, double refracting prisms, glittering like silk or diamonds. The end surfaces are inclined at about 120° to the prism edges.

0·2417 grm. of substance after repeated evaporation with sulphuric acid: 0·1394 grm. $PbSO_4$. 0·1716 grm. substance: 0·3550 grm. CO_2; 0·0648 grm. H_2O.

$PbC_{24}H_{20}$: Calculated—Pb, 40·03; C, 56·14; H, 3·90.
Found—Pb, 39·40; C, 56·35; H, 4·19.

Clearly this lead tetraphenyl is identical with the substance obtained by Polis (*Berichte*, 1887, xx., 717, 3331), by boiling lead sodium with bromobenzene and acetic ether for 3 days.

The use of phenyl magnesium bromide in our method, apart from the very simple process and the good yield (if the reagents are quite dry), has the great advantage that the lead chloride is used directly and is not exposed to the risk of loss on converting it into the metal, which is a very important point when the cost of concentrated radio-lead chloride is taken into account. Also this application of Grignard's reaction, as our preliminary experiments showed, can be used very generally in order to obtain phenyl compounds or their ethereal solutions in the cases when the metals yield no such compounds. ($BiCl_3$, $SuCl_4$, and $SiCl_4$ readily form phenyl compounds). In particular, the noble metals, gold, silver, and platinum, can be converted into beautiful coloured ethersols, upon which a full report will shortly be made.

Lead tetraphenyl itself calls for closer investigation from many points of view. Thus when the crystals are dissolved in a mixture of 3 volumes of concentrated sulphuric acid to 1 volume of fuming nitric acid, an intense brownish-red colouration appears, afterwards changing to cherry-red. If after longer action this is precipitated with much water at the ordinary temperature, fine white pointed prisms united in branching feathery formations crystallise; these swell up on heating, giving a strong smell like nitro-benzene.

The method of phenylation is too dear for working up lead chloride which has not been concentrated, but it presents very considerable advantages in removing the ordinary inactive lead from RaD preparations, enriched by distillation with ammonium chloride, electrolysis, or by crystallisation.

RaF, in consequence of a secondary reduction, goes into the residue, RaD also for the most part remains behind, RaE is found in the deposit of magnesia separating on shaking up the benzene solution with water, and very feebly active lead goes over into the phenyl compound. The following table shows the result of the concentration of RaD.

Uranium units.

I.	
Sulphate from the residue (after removing RaF as completely as possible), three weeks after separation	15
Sulphate from the residue six weeks after separation	36
Sulphate from the phenyl compound three weeks after separation	2
Sulphate from the phenyl compound six weeks after separation	0·8
II.	
Sulphate from the residue (after removing RaF as completely as possible), three weeks after separation	23
Sulphate from the residue six weeks after separation	42
Sulphate from the phenyl compound three weeks after separation	7
Sulphate from the phenyl compound six weeks after separation	0·5

Even if these numbers are not absolutely valid owing to the amounts of RaE_1 and RaE_2 which are not taken into account, they show that in the part not converted into the phenyl compound (the residue), the principle producing activity (which must be the RaD) appears very decidedly concentrated. If the residue is again treated as chloride with phenyl magnesium bromide in ether and benzene, the oxygen of the air takes part in the reaction and an intense fuchsine-red colouration is produced, which is destroyed by moisture.

The aim of our next experiments will be to investigate the subject more fully in the directions we have indicated in this paper.—*Berichte*, 1907, xl., 2425.

Chemistry of Silicon.—A. Ladenburg.—If silicon tetraphenyl is warmed on a water-bath with bromine and then heated in a tube for eight to ten hours with 10 per cent bromine to 150°, the following reaction occurs:—$Si(C_6H_5)_4 + Br_2 = C_6H_5Br + Si(C_6H_5)_3Br$. The contents of the tube are washed out with ligroin, which is evaporated off on the water-bath, and the bromo-benzene is driven off *in vacuo*. The impure bromide crystallises out on cooling, and may be purified by dissolving in ether. Triphenyl silicon bromide is a colourless crystalline substance fuming in air and melting at 118—120°. When it is heated with potash solution to 120° it yields the triphenyl silicol, $Si(C_6H_5)_3OH$. When this silicol is dissolved in fuming sulphuric acid, the liquid is poured into cold water and neutralised with barium carbonate, after warming for some time crystals of the barium salt of the trisulpho acid of triphenyl silicol separate: $Si(C_6H_4SO_3Ba)_3OH$. Diphenyl silicon dibromide, $Si(C_6H_5)_2Br_2$, cannot be prepared directly from silicon tetraphenyl, but the monobromide when heated with bromine yields an oil from which it may be separated. Zinc ethyl acts upon the dibromide giving silicon diphenyl diethyl, and with water the dibromide gives an oil which has approximately the composition represented by the formula $Si(C_6H_5)_2O$. Zinc ethyl with triphenyl silicon bromide gives two compounds, triphenyl silicon hydride, $Si(C_6H_5)_3H$, and ethyl triphenyl silicon.—*Berichte*, xl., No. 9.

CONTRIBUTIONS TO THE CHEMISTRY OF GOLD.*

By F. H. CAMPBELL. M.Sc. (Melbourne).

That revision of and additions to our knowledge of the chemistry of gold is necessary is obvious to any one who refers to the literature of the subject. In many cases different investigators have obtained contradictory results, and other observations have been recorded which have not been contradicted solely because the work has never been repeated.

In any case, investigations in which the methods of physical chemistry are applied are entirely wanting. It was a consideration of these facts which led to the following research. The main part of the work deals with the halogen compounds, but in addition the normal potential of $Au^{\cdot}$ ions was determined.

The Properties of AuI.

This substance has long been known, having been prepared indirectly by Fordos and others (*Journ. Pharm.*, xxvii., 653; *Comptes Rendus*, cxxxix., p. 733). It was first synthesised from its elements by Meyer and obtained in a crystalline form. The method used which gave the largest yield of crystals was to shake precipitated gold with a solution of iodine in KI; after shaking had been continued for from sixteen to twenty-four hours, crystals were observed to have formed. These were lemon-yellow in colour. The temperature of the thermostat was 25° C.

The dissociation pressure of AuI must be smaller than the normal pressure of iodine at the same temperature, since had it been greater the substances would not have united. It remained to determine with what pressure of iodine this substance and gold are in equilibrium.

This equilibrium pressure can be approached from both sides; if metallic gold is brought into contact with iodine, the pressure of which is greater than that of AuI, the substances will unite until the pressure reaches the equilibrium value; on the other hand, AuI, when brought into a space in which the pressure is less than this pressure, will dissociate until equilibrium is established as before.

Since, as will be shown, this pressure at 25° is but little below that of pure iodine, the fact that the aurous iodide decomposes rapidly into its elements when exposed to the air is explained.

As in the case of the dissociation of $CaCO_3$, so in the action $2AuI = 2Au + I_2$ we have to do with a univariant system consisting of the two solid phases, AuI and Au, and the gaseous I_2. There is only one variable, namely, the pressure of iodine, which is dependent on the temperature.

The method of experiment was similar to that used by Stromholm, Hamburger and Abegg, and Maitland and Abegg for the formation of various polyiodides (*Journ. Prakt. Chem.*, lxvi., 67; *Zeit. Anorg. Chem.*, 1906, xlix., p. 341). The iodine was dissolved in CCl_4, in which AuI, as well as Au, are insoluble, and in which iodine is in the same state of molecular aggregation as it is in the gas form; hence according to Henry's law the gaseous pressure of iodine above the solution is directly proportional to the concentration of the dissolved iodine.

Solutions of iodine of varying concentrations were placed in bottles having well-fitting glass stoppers together with finely divided gold. After having covered the stoppers with rubber caps, the bottles were shaken for seven days in a thermostat at 25° C. Those solutions the original concentration of which did not reach 0·1088 mol. of I_2 per litre, had exactly the same titre afterwards as before, while those with a higher original concentration than this became diluted to 0·1088 mols. per litre. The iodine estimations were performed in the usual way with 0·1*N* $Na_2S_2O_3$, starch being used as an indicator. 1 cc. of the CCl_4 solution was placed in a stoppered bottle so that the two solutions could be shaken together. By this means a sharp end-point could be obtained.

In other cases AuI was prepared by precipitation from $AuCl_3$ solution by means of KI, $AuCl_3$ being always in excess. The mixture of AuI and I_2 thus obtained was washed with cold water and dried with filter-paper before being shaken with a dilute iodine solution. Again the solutions obtained from the first series of experiments were diluted with pure CCl_4. It was found that under the conditions of experiment the action $2Au + I_2 \rightleftarrows 2AuI$ goes at a much greater rate from left to right than the reverse action. For example,—

Table I.—*Action of Iodine in* CCl_4 *on* Au *metal.*

$Na_2S_2O_3$ required by 1 cc. solution.	Duration of experiment.
Cc.	Days.
2·24	0
2·24	3
2·25	10
2·26	16
2·24	30
2·26	60

After each titration 2 cc. of iodine solution, the titre of which was 2·40, was added. This table not only serves to show the great constancy obtained, but also that the action goes comparatively quickly. On the other hand, Table II. shows that when AuI is placed in contact with a dilute iodine solution the action is exceedingly slow.

Table II.—*Action of Solvent* CCl_4 *on* AuI.

$Na_2S_2O_3$ required by 1 cc. solution.	Duration of experiment.
Cc.	Days.
2·03	0
2·08	8
2·10	42
2.11	64

Since in this particular case the amount of AuI originally present was small, the constancy of the last results may be attributed to the total decomposition of this substance.

In another case about 1 grm. of AuI was prepared by precipitation as above. In order to hasten the action various methods were tried; the most effective was found to be to treat the solution for some hours to 55° and then to shake for some days at 25°. From an experiment conducted in this way, the results given in Table III. were obtained.

Table III.

$Na_2S_2O_3$ required by 1 cc. solution.	Duration of experiment.
Cc.	Days.
2·08	0
2·14	9
2·21	21

Taking the mean of the values obtained by both methods we find that 1 cc. of the solution requires 2·23 cc. 0·1*N* $Na_2S_2O_3$, so that a solution of iodine in CCl_4 containing 0·1088 mol. I_2 per litre is in equilibrium with gold and AuI at 25°. Under these conditions a saturated solution contains 0·1156 mol. iodine, hence the pressure of gaseous iodine which is in equilibrium with AuI and gold is $\frac{0\cdot1088}{0\cdot1156} = 0\cdot943$ of that of pure iodine.

Therefore any solution of iodine is or is not able to act on gold according to whether it is or is not 0·943 saturated.

* A Paper read before the Faraday Society, May 28, 1907.

The Determination of the Formula of the Double Iodide of Potassium and Gold.

When excess of gold is treated with iodine dissolved in aqueous solutions of KI, part is converted into AuI, which is insoluble, part remains unattacked, while the rest is dissolved.

The action may also be looked at from the point of view of the iodine. Of this, part combines with I′ ions to form I_3' ions, part goes to form AuI, part is used to form a complex gold-containing anion, while the rest, relatively to the other parts very small, remains as free molecular iodine, I_2.

Of the AuI formed part remains insoluble, while the rest combines either with only Iodine ions, I′, to form a complex anion, probably AuI_2', or else with iodine ions, I′, and free iodine, I_2, to form a complex ion, probably AuI_4'; in other words, the complex compound may contain either mono- or tri-valent gold. In order to solve the problem the following experiments were made.

Meyer has shown that AuI is formed under the conditions of experiment, but it was considered advisable to analyse the crystalline substance obtained, since this decomposes rapidly on washing. Exact analysis was not possible. The results obtained, however, left no doubt that the substance obtained is AuI.

It was found that when a glass rod, previously roughened by treatment with HF, and of such a length that it could not move, was placed in the bottle, good crystals were formed upon it. When required for analysis, the crystals were removed, washed with cold water, dried with filter-paper, and transferred to a tared glass tube, the neck of which was then sealed off, the tube and contents were weighed; the neck was next broken and the tube gently heated till iodine vapour ceased to be evolved. After cooling in a desiccator the tube was again weighed.

In one case the following results were obtained:—

Weight of substances before heating ..	0·0012
Weight of substances after heating ..	0·0007
Iodine volatilised	0·0005
Percentage of iodine (found)	41·7
Percentage of iodine (calculated)	39·5

In this case the crystals had evidently not been thoroughly dry, but in any case, owing to the unfortunate necessity of using exceedingly small quantities, a higher degree of accuracy is not to be expected.

It having thus been proved that the solid phases present are Au and AuI we are in a position to say what we have in the two systems present in solution. We have I_2, I′, I_3', Au·, Au···. and the complex ions either AuI_2' or AuI_4'. Of these I_2, Au·, Au··· are present in very small quantity, so that the dissolved gold may be considered as being present completely in the form of complex anion, and we make the assumption that the complexes have only one formula, either $Au^{I}I_2'$ or $Au^{III}I_4'$.

According to the law of mass action,—

$$\frac{(I_2)\cdot(I')}{(I_3')} = Kj;$$

and since—

$$AuI + I' = AuI_2' \quad \text{or} \quad AuI + I' + I_2 = AuI_4',$$

then—

$$\frac{(AuI_2')}{(AuI)(I')} = K_1 \quad \text{or} \quad \frac{(AuI_4')}{(AuI)(I_3')} = \frac{(AuI_4')\cdot Kj}{(AuI)(I_2)(I')} = K_2.$$

(Formulæ in brackets mean their mol. concentrations).

The value of Kj is known from the work of Jakowkin (*Zeit. Phys., Chem.*, xx., 19); it is sufficient to determine its value in the solutions under consideration to ascertain whether ther value K_1 or K_2 is the equilibrium constant among the other constituent of the solution, since Kj and K_1 or K_2 are mutally interdependent. Since this has been proved to be so in another case by Maitland and Abegg, the direct determination of the complex constant K_1 or K_2 was considered to be unnecessary.

The method of procedure was as follows:—Equal quantities of CCl_4 and aqueous KI solutions almost saturated with iodine were placed in bottles in contact with excess of pure precipitated gold. The mixture was then shaken in a thermostat at 25° until equilibrium was reached, which happened in seven or eight days. The course of the reaction was followed by pipetting out quantities of 1 cc. of the CCl_4 solution and titrating with 0·1*n* $Na_2S_2O_3$. When the duration of the experiment had been determined, only one preliminary estimation—on the sixth day—was performed.

Equilibrium having been reached, 5 cc. of the CCl_4 solution was pipetted out and titrated as before; the value obtained was divided by the distribution coefficient of iodine between CCl_4 and water at 25°, namely 85; this gave the quantity of I_2 present in the aqueous solution.

5 cc. of the aqueous solution were evaporated to dryness in a porcelain dish over a water-bath, the brown residue was further heated over a small flame until the evolution of iodine ceased, the residue was then treated with water and the gold was finally washed on a small ashless filter. When pure the paper was dried and burnt and the residual gold weighed. From its quantity the quantity of iodine combined with gold was calculated.

A further portion of 5 cc. of the aqueous solution was taken for the determination of the total titratable iodine, that is I_2 (giving 2I), I_3' (giving 2I), AuI_2' (giving 1I besides gold), and AuI_4' (giving 3I besides gold). It was found that direct titration of the solution gave unsatisfactory results, owing to a reaction between gold and $Na_2S_2O_3$. The difficulty was overcome by distilling the iodine into a known volume of 0·1*n* $Na_2S_2O_3$ and titrating back with 0·1*n* iodine solution.

In order to determine Kj we use the value for the concentration of I_2 found as described above; the concentration of I_3' is obtained by subtracting from the total titratable iodine in aqueous solution the amount of free I_2 and the amount of iodine combined with gold, while the concentration of I′ is obtained by subtracting I_3' from the concentration of I′ which was originally in solution.

Jakowkin obtained for Kj values varying between $0{\cdot}77 \times 10^{-3}$ and $1{\cdot}4 \times 10^{-3}$. It will be seen from Table IV. that the values obtained for Kj, though a little too high, agree fairly well with those of Jakowkin when the gold is assumed to enter the complex in the monovalent condition, while when the presence of trivalent gold is assumed the constant is not at all concordant with that of Jakowkin. The values vary in the same direction as those of Jakowkin, the value of Kj is lower in the more concentrated solutions than in the dilute ones. The variation of the free iodine as shown in column V. was only slight in our experiments. As the comparison between the above formulæ for K_1 and K_2 shows, a greater variation of the free iodine would give another good way to show that our conclusion is right.

The Properties of Aurous Chloride.

The literature of AuCl is scanty and contains many contradictory statements, so the substance was prepared and examined.

The method of preparation was the usual one. Pure, dry $AuCl_3$ was prepared by passing over pure dry gold chlorine purified by passing through $CuSO_4$ solution, and dried by passing through two wash-bottles containing concentrated sulphuric acid, and a tower containing pumice soaked in sulphuric acid. The temperature was kept between 200° and 220°.

The course of the action was followed by weighing the tube containing the gold or the chlorine as the case might be. It was found that though the absorption of chlorine was at first rapid, it afterwards became exceedingly slow, and in no case was pure $AuCl_3$ obtained. Since the presence of AuCl or Au, the only possible impurities, could not have any disturbing effects at a later stage, special measures to drive the chlorination to completion were not taken.

TABLE IV.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.	XII.
							For AuI_3'.			For AuI_3'.	
No.	Mol. KI per litre water.	Atoms iodine per litre water, "titratable iodine."	Mol. gold per litre water.	Mol. iodine per litre water, "free iodine" VI. $\times \frac{1}{85}$.	Mol. iodine per litre CCl_4. (a)	III.—IV. 2 Mol. I_2+I_3' per litre.	VII.—V. Mol. I_3' per litre.	(II.—VIII.)—V. VIII. = Kj.	III.—3IV. 2 Mol. I_2+I_3' per litre.	X.—V. Mol. I_3' per litre.	(II.—XI.)—V. XI. = Kj.
1.	0·1009	0·0842	0·0089	$1·09 \times 10^{-3}$	0·0932	0·0376	0·0365	$1·92 \times 10^{-3}$	0·0288	0·0277	$2·89 \times 10^{-3}$
2.	0·1009	0·0964	0·0106	1·13 "	0·0962	0·0429	0·0418	1·59 "	0·0323	0·0312	2·52 "
3.	0·1009	0·0910	0·0091	1·07 "	0·0912	0·0409	0·0399	1·63 "	0·0318	0·0308	2·43 "
4.	0·1009	0·0970	0·0099	1·07 "	0·0907	0·0435	0·0425	1·47 "	0·0336	0·0326	2·24 "
5.	0.2508	0·2616	0·0290	1·16 "	0·0988	0·1163	0·1152	1·36 "	0·0873	0·0862	2·21 "
6.	0·2508	0·2556	0·0297	1·06 "	0·0902	0·1129	0·1119	1·31 "	0·0832	0·0822	2·17 "
7.	0·4038	0·3839	0·0565	1·03 "	0·0882	0·1637	0·1627	1·52 "	0·1072	0·1062	2·88 "
8.	0·4038	0·4009	0·0489	1·10 "	0·0942	0·1760	0·1749	1·44 "	0·1271	0·1260	2·42 "
9.	0·4038	0·3959	0·0522	1·12 "	0·0952	0·1718	0·1707	1·53 "	0·1196	0·1185	2·69 "
10.	1·0096	0·9482	0·1199	0·96 "	0·0817	0·4142	0·4132	1·39 "	0·2943	0·2933	2·34 "
11.	1·0096	1·1111	0·1142	1·07 "	0·0912	0·4984	0·4974	1·10 "	0·3842	0·3832	1·75 "

(a) Since 0·1088 is the lowest possible concentration for the stability of AuI, as shown above, it was here in an unstable condition, which could be realised because of the great slowness of the AuI decomposition.

The substance obtained in this way was a dark red crystalline mass, and needle-like crystals of the same colour always formed in the cooler parts of the tube.

The temperature was allowed to fall to between 170° and 180°, and was kept between these limits during the subsequent dechlorination. The tube used in these operations was of such a kind that during heating it could be almost evacuated by means of a suction pump. The removal of the evolved chlorine was facilitated by the passing of a very slow stream of dry air. By this means 4 to 5 grms. of $AuCl_3$ could be converted into AuCl in seven or eight hours. The dechlorination was checked by weighing, and the action was stopped when the weight was approximately that theoretically required for AuCl. The temperatures given by different authors as the most suitable for the formation of AuCl vary between 120° and 200°. With respect to the lower temperatures it may be stated that the crystals which, as was mentioned, formed in the upper part of the tube, did not change colour nor lose their crystalline form as did those in the more strongly heated part of the tube. This would seem to show that at temperatures below 140° to 150° the rate of reaction is exceedingly slow.

The substance so obtained was washed with ether until the last washings showed no trace of colour, the solution of $AuCl_3$ in ether being of a strong yellow colour. It was found that unless the ether had been distilled over sodium a short time before use, it was impossible to wash the AuCl out, thus showing the extreme ease with which water reacts with AuCl.

It was found that when a portion of the substance had been washed pure with ether and was allowed to stand in a stoppered bottle for a day, it again showed evidence of the presence of $AuCl_3$ on being treated with ether. Since the reaction might have been due to the presence of traces of water, fresh experiments were made. The substance was washed as before, and when clean placed in a desiccator containing phosphorus pentoxide. After two days the presence of $AuCl_3$ was obvious when ether was placed in the tube. It was thus shown that the action $3AuCl = AuCl_3 + 2Au$ takes place at ordinary temperatures and in absence of water.

As is to be expected this action goes on rapidly at higher temperatures. The substance when placed in a tube, sealed up and heated, always gave a red sublimate of $AuCl_3$, though proved to be free of this substance by the ether test immediately before experiment.

Dry chlorine and AuCl combine readily at ordinary temperatures to form $AuCl_3$:—$AuCl + Cl_2 = AuCl_3$.

AuCl was placed in a small bulb to which was attached a capillary tube containing a thread of concentrated H_2SO_4, the whole apparatus was filled with pure dry chlorine, and allowed to stand. A steady decrease in volume took place, shown by the movement of the manometer thread; that $AuCl_3$ was formed was shown by heating the substance, when the quantity of $AuCl_3$ which sublimed was much larger than could be accounted for by the decomposition of the AuCl.

The Properties of Aurous Bromide.

AuBr is readily prepared by gently heating $AuBr_3$. Obtained in this way it is a brown powder. It may also be prepared by simply allowing $AuBr_3$ to stand in the air.

Like the corresponding chloride, AuBr decomposes thus—

$$3AuBr = AuBr_3 + 2Au$$

in a dry atmosphere at ordinary temperature, but to a less extent, while on heating the action is rapid.

That $AuBr_3$ does decompose into AuBr at ordinary temperatures was shown by the fact that the substance took the distinctive colour of AuBr. In other words, the decomposition of $AuBr_3$ to form AuBr takes place more rapidly under the conditions of experiment than does that of AuBr to form $AuBr_3$.

(To be continued).

PREPARATION OF THE ANILINE DERIVATIVES OF SUCCINIC ACID AND OF PHTHALIC ACID.

By J. BISHOP TINGLE and MARSHALL P. CRAM.

In the course of some work on the nitration of certain aniline derivatives, which is being carried out by one of us in conjunction with Mr. F. C. Blanck in the laboratory of the Johns Hopkins University (*Am. Chem. Journ.*, 1906, xxxvi., 605), it was necessary to prepare fairly large quantities of the aniline compounds of succinic and phthalic acids. Some of the methods which we have employed for this purpose differ in certain respects from those described in the literature; in two cases they are entirely new; moreover, they have all proved to be thoroughy satisfactory and adequate for our purpose; consequently it appears to be desirable to place them on record.

Succinanil, $\begin{matrix}CH_2.CO\\ |\\ CH_2.CO\end{matrix}\!\!>\!NC_6H_5$, was prepared essentially according to the method of Menschutkin (*Liebig's Ann. Chem.*, 1872, clxii., 166), but the mixture of acid, 45 grms., and aniline 40 grms., was placed in a small retort and heated for three to four hours, at 140—150°, in a paraffin-bath. By this means the water was steadily eliminated, and there was absolutely none of the "bumping" which was a source of trouble to Menschutkin. As soon as the action is completed, the retort is removed from the bath and quickly heated by a direct flame. A little aniline and water pass over, and then the anil. If the distillation is conducted as rapidly as possible there is no danger of the retort's neck becoming closed. The yield is practically quantitative; from 270 grms. of the acid we obtained 330 grms. of anil, once re-crystallised from alcohol.

The conversion of succinanil into *succinanilic acid*, $C_6H_5NHCOCH_2CH_2COOH$, was carried out according to the directions of Menschutkin (*Liebig's Ann. Chem.*, 1872, clxii., 178), by heating the anil with milk of lime, in slight excess. Vigorous boiling for ten or fifteen minutes is necessary to bring the calcium salt into solution. The crystals which form on cooling are separated, treated with hydrochloric acid, and the precipitated anilic acid is re-crystallised once from water. The yield is 129 grms. of purified material from 200 grms. of anil.

Laurent and Gerhardt discovered *succinanilide*, $C_6H_5NHCOCH_2CH_2CONHC_6H_5$, as a by-product in the preparation of succinanil (*Ann. Chim. Phys.*, 1848, [3], xxiv., 179; *Liebig's Ann. Chem.*, 1848, lxviii., 29). Menschutkin (*Liebig's Ann. Chem.*, 1872, clxii., 187), who repeated their work, found that, contrary to the statement of Laurent and Gerhardt, one re-crystallisation from alcohol was quite inadequate for the purification of the substance. He accomplished this by the use of alcoholic potassium hydroxide, which readily acts on the anil, but leaves the anilide unchanged. The yield is very poor. Laurent and Gerhardt only isolated a "small quantity," and Menschutkin obtained 22 grms. of crude material from 40 grms. of acid and 70 grms. of aniline. We find that the anilide can be easily prepared by heating succinanilic acid, 50 grms., with aniline 40 grms., in a reflux apparatus at 180°, during five working days. The product was treated twice with excess of cold dilute hydrochloric acid to remove the unchanged aniline, and, after being washed with water, was boiled for about five minutes with a clear filtered potassium hydroxide solution, consisting of 12 grms. of stick potash in 250 cc. of 95 per cent alcohol, to dissolve any succinanil and succinanilic acid which might be present. Finally, it was re-crystallised from alcohol. The yield was 17·1 grms. of purified material, *i.e.*, 24·8 per cent of the theoretical quantity. We think that the yield might have been improved by heating the mixture of succinanilic acid and aniline under pressure, but a steel bomb was not available, and the use of sealed tubes would have involved a good deal of extra trouble. Some little time after the completion of this part of our work, Arnold Reissert and Arnold More (*Ber.*, 1906, xxxix., 3300) described a method of preparing malonanilide by boiling ethyl malonate with aniline for a short time, and then distilling off the alcohol as it is produced. They do not appear to have tested the behaviour of ethyl succinate under these conditions. We are indebted to Mr. H. N. Morse for carrying out an experiment with ethyl succinate and aniline, according to the method of Reissert and More. After boiling these substances for about thirty minutes with a reflux condenser, the condenser was reversed and the material slowly distilled. The heat was applied by means of a bath containing sulphuric acid. The distillate consisted chiefly of aniline, in quantity almost equal to that originally used. The residue contained a relatively large amount of ethyl succinate, together with a small quantity of solid. The results of this experiment indicate, therefore, that the procedure of Reissert and More is not applicable to ethyl succinate, and that our method for preparing succinanilide is superior to any which has hitherto been described.

Preparation of the Aniline Derivatives of Phthalic Acid.

Of the various methods which have been suggested for the preparation of *phthalanil*, that of Zincke and Cooksey appeared to us to be the most convenient (*Liebig's Ann. Chem.*, 1889, cclv., 375). It consists in adding the necessary quantity of aniline to a glacial acetic acid solution of phthalic acid, and allowing the mixture to remain for some hours at the ordinary temperature. When we attempted to carry out this experiment we found that the solubility of phthalic acid in glacial acetic acid is so very small, being only about 1·7 grms. in 100 grms. at the ordinary temperature, that the preparation of the quantity of material which we needed would have involved a relatively very large expenditure of time and acetic acid. Our experiments were therefore conducted as follows:—Phthalic acid, 200 grms. = 1 mol. and glacial acetic acid, 500 grms., were mixed, and aniline, 112 grms. = 1 mol., was added. After heating this material on a water-bath during two working days, water was added, and the product filtered. The residue consisted of a mixture which could not be separated by repeated extraction with alcohol. In these circumstances, the portion which had not dissolved in alcohol and the part which deposited on cooling the alcoholic solution were mixed, and boiled for ten minutes with a solution of 20 grms. of dry sodium carbonate in 500 cc. of water. A portion dissolved; the remainder, after being washed and dried, weighed 100 grms. and melted at 203—206°; it was therefore practically pure phthalanil, for which Zincke and Cooksey (*loc. cit.*) gave the melting-point 203° and Döbner 205° (*Liebig's Ann. Chem.*, 1881, ccx., 267). The former chemists omit all reference to the yield which they obtained, whereas the latter reports a "theoretical yield" by the distillation of phthalic anhydride and aniline. The yield by our method, as already noted, is 50 per cent of the phthalic acid employed, and if we were repeating our preparation we should omit the treatment with alcohol and boil the precipitate from the diluted acetic acid directly with sodium carbonate. Even with this simplification our method does not appear to be as good as Döbner's, though it is decidedly superior to that of Zincke and Cooksey. There is no indication in the paper of their reason for ignoring Döbner's method, but they state distinctly that "heating should be avoided." Having obtained all the material which we needed we did not consider it necessary to repeat Döbner's work. If there is ground for distrusting it, then our method appears to be the best and most convenient hitherto suggested for the preparation of phthalanil.

At a later stage of our investigation we found that phthalanilic acid could be easily prepared from its constituents without the use of a solvent. Phthalic acid, 10 grms., and aniline 14·6 grms. = about 2·25 mols., were mixed, and allowed to remain at the ordinary temperature for twenty-two minutes. The flask was found to have become hot, and steam had condensed in its upper portion;

moreover, the mixture had become very stiff. More aniline, 6·7 grms., was now added, and the substance heated on a boiling water-bath. After seven minutes a portion was removed, washed with cold alcohol, and re-crystallised from more alcohol. At first the solution was pink, but it became yellow as the heating continued. The product melted at about 160°, re-solidified, and melted again at 190—195°; it contained a considerable proportion of nitrogen, as shown by the sodium test. A portion which had been washed, but not re-crystallised, behaved in a similar manner. The heating was continued for four hours on the water-bath, and another portion withdrawn; after purification in the manner described it gave the same results. A further five hours' heating, nine hours altogether, gave a product which was chiefly phthalanilic acid, but the alcoholic washings, containing, of course, the excess of aniline, after standing for a time at the ordinary temperature, deposited phthalanil. This is certainly the easiest method known to us for making phthalanilic acid, and the yield appeared to be very good. We did not investigate the matter further because we had already obtained as much of the acid as we required. We refer later to the readiness with which phthalanil is formed from phthalanilic acid in the presence of an excess of aniline.

Phthalanilic acid was obtained without difficulty from phthalanil by the method of Zincke and Cooksey (*Liebig's Ann. Chem.*, 1889, cclv., 375), which consists in treating the phthalanil with alcoholic potassium hydroxide and acidifying the resulting potassium salt. Our product melted at 164°, re-solidified, and melted again at 204°, showing that at its melting-point this acid is changed into phthalanil. The yield was 25·5 grms. of acid from 73 grms. of phthalanil.

We carried out a considerable number of experiments with aniline and phthalic and phthalanilic acids respectively, with the object of preparing *phthalanilide*, either in the manner employed for obtaining succinanilide (see above), or directly from the constituents. It was quickly evident that the anilide is relatively highly unstable, and like the anilic acid, is very readily transformed into the anil. We tried careful regulation of the temperature, with and without the use of aniline in excess. We obtained the phthalanilide in several experiments, but on repeating them it became manifest that this result was dependent on conditions beyond ordinary control, and, consequently, we cannot regard the problem as being solved at all to our satisfaction. We give below a brief description of our experiments. In the preparation of phthalanil by the method of Zincke and Cooksey (*loc. cit.*), we separated the products of the reaction by means of sodium carbonate. On acidification a white precipitate was formed consisting, presumably, of phthalic and phthalanilic acids (see above). This mixture was added to enough aniline to form a stiff paste, and heated on a water-bath for about two weeks. A portion of the product, washed twice with cold dilute hydrochloric acid, and then re-crystallised from alcohol, melted at 230°, which is 1° below the melting-point of phthalanilide. The remainder of the aniline mixture was now heated at 140° for three or four days, and was then found to consist of phthalanil.

In another experiment, phthalic acid, 9 grms., and aniline 22 grms., were heated on the water-bath for two days. The product was purified by means of hydrochloric acid and alcohol, as described above, and melted at 215—220°. The melting-points of phthalanil and of phthalic acid are 203° and 213°, respectively. Boiling for six hours with alcohol, or prolonged heating on the water-bath with an additional quantity of aniline, caused no change in the melting-point of the product. A further 5 grms. of aniline were now added and the mixture heated at 120—130°, for 1·5 days. The product melted at 201—205°, showing it to be, essentially, phthalanil.

Phthalanilic acid, 5 grms., and aniline 12·5 grms., were heated at 120—310° for 1·5 days; the product melted at about 201° and further heating of the mixture at 140—190° produced no decided change in this respect. Additional experiments were made with similar mixtures of phthalanilic acid and aniline, at temperatures ranging from that of the room up to the one given by a boiling water-bath. In some cases the product was re-crystallised from alcohol, in others washed with cold alcohol or with cold hydrochloric acid. The substances obtained consisted either wholly of phthalanil or of mixtures of this with phthalanilic acid; moreover, we found that boling the alcoholic washings, containing aniline and phthalanilic acid, always resulted in the formation of phthalanil.

A similar series of experiments was carried out with phthalic acid and aniline, but we failed to obtain any of the anilide. We found, however, that phthalanilic acid, as already stated, is easily prepared by simply mixing phthalic acid (1 mol.) with aniline (2·5 mols.) at the ordinary temperature.

We think our results indicate that, although the formation of succinanilic acid and of phthalanilic acid take place in a similar manner, yet in the presence of aniline the further reaction of these substances is quite different, the former yielding succinanilide and the latter phthalanil; moreover, this difference is not by any means simply a question of relative stability at a given temperature, because, as our experiments show, phthalanilic acid is more unstable at the temperature of a boiling water-bath, in the presence of a large excess of aniline, than in its absence. One experiment in support of this has already been given and two others may be cited. Phthalic acid, 10 grms., was mixed with aniline 14·6 grms. = about 2·25 mols., and as it became thick more aniline, 6·7 grms., was added and the mixture heated in an open flask, on the water-bath, for ten hours. After being washed with cold alcohol the solid residue was found to consist of phthalanilic acid. The alcoholic washings containing the aniline, without any further heating, soon deposited phthalanil. During a further five hours' heating the contents of the flask were accidentally allowed to become dry, as the excess of aniline is readily volatile in the steam formed during the reaction. The product was still phthalanilic acid. It was now moistened with aniline, allowed to remain at the ordinary temperature over Sunday, and then heated on the water-bath for a working day (eight hours). This treatment converted it completely into phthalanil.

The second experiment, illustrating the same point, is as follows:—Phthalanilic acid, 3 grms., was mixed with enough aniline to form a thick paste and heated on a boiling water-bath for two minutes. A portion was removed, washed with cold alcohol, and dried. It melted at about 145°, resolidified, and then melted at about 200°, showing that it was unchanged phthalanilic acid. The alcoholic washings, after being concentrated, deposited phthalanil. The flask having been off the water-bath for thirteen minutes was now re-heated for two minutes and a portion of the product tested. It behaved exactly like the first specimen. The flask having been off the bath for twelve minutes was now again heated for six minutes. The product was phthalanil. Eleven minutes' additional heating produced no further change. It may be mentioned that the solubility of phthalanil in alcohol is altogether too slight for it to have been removed from the product of the reaction by washing at the ordinary temperature, and that it must, therefore, have been formed in the wash liquors. These experiments show that, whereas fifteen hours' heating an the water-bath and one night's standing at the ordinary temperature is not sufficient to convert phthanilic acid into phthalanil in the absence of excess of aniline, yet in the presence of such an excess the change is complete after ten minutes' heating and twenty-three minutes' standing.

The phthalanilide which we required was finally prepared from aniline and phthalyl chloride, according to the method of Rogrow (*Ber.*, 1897, xxx., 1442). After re-crystallisation from alcohol it melted at 232—233°, the temperature given in the literature being 231°.

The phthalyl chloride was obtained essentially according to the method of Claus and Hoch (*Ber.*, 1886, xix., 1187),

and of Graebe (*Liebig's Ann. Chem.*, 1887, ccxxxviii., 329). Phthalic anhydride, 50 grms. = 1 mol., was mixed with powdered phosphorus pentachloride, 70 grms. = 1 mol., and heated in a reflux apparatus at 120—170°, during eight hours. Inadvertently, the temperature was allowed to rise for a short time to 210°. The phosphorus oxychloride was volatilised under the ordinary pressure and the residue distilled; it boiled at about 47° (130 mm.). After standing for an hour the distillate deposited crystals which were proved to consist of unchanged phthalic anhydride; they were removed by filtration and the liquid chloride gradually added to an alcoholic solution of aniline, in the manner indicated above. The yield of purified chloride was 22·6 grms. and about 22 grms. of unchanged phthalic anhydride were recovered. The above experimental conditions offer the great advantage of yielding a product which is apparently entirely free from chlorine substitution products isomeric with phthalyl chloride, and from phthalyl tetrachloride. These substances were encountered by the chemists mentioned above, and their separation caused a good deal of trouble and loss of material. We attribute our success chiefly to the distillation of the crude material under reduced pressure, and believe that the yield of phthalyl chloride could be improved by the use of a larger proportion of phosphorus pentachloride, without much danger of the formation of isomeric chlorine compounds. The work is being continued by one of us in conjunction with Mr. Lovelace.—*American Chemical Journal*, xxxvii., No. 6.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 20th, 1907.

Sir William Ramsay, K.C.B., F.R.S., President, in the Chair.

(Concluded from p. 10).

139. "*The Oxidation of Hydrazines by Free Oxygen.*" By Frederick Daniel Chattaway.

Hydrazines of the formula $R{\cdot}NH{\cdot}NH_2$, where R is a cyclic group, are readily oxidised by free oxygen, the action being accelerated in a remarkable way by alkali hydroxides. In the case of phenylhydrazine dissolved in about three times its weight of 4N-alcoholic potash, oxidation is so rapid that the liquid effervesces freely from escape of nitrogen on mere exposure to the air.

The action appears to be a general one, and results in the liberation of nitrogen and the replacement of the $NH{\cdot}NH_2$ group by hydrogen, thus: $R{\cdot}NH{\cdot}NH_2 + O = R{\cdot}H + N_2 + H_2O$.

It is simply explained by assuming that when such a hydrazine is oxidised, an unstable hydroxyhydrazine is first produced, which at once decomposes, thus:— $R{\cdot}HN{\cdot}NH_2 \rightarrow R{\cdot}HN{\cdot}NH{\cdot}OH \rightarrow RH + N_2 + H_2O$.

The action which takes place in the oxidation of hydrazines is thus closely connected with those reactions of diazonium compounds in which the diazonium group is replaced by hydrogen.

140. "*Calmatambin: a New Glucoside.*" By Frank Lee Pyman.

The author described the isolation of a new glucoside, *Calmatambin*, from the bark of a tree indigenous to West Africa, which is known to the natives as *Calmatamba*, and is probably identical with *Canthium glabrifolium*.

The glucoside has the formula $C_{19}H_{28}O_{13},2H_2O$, and crystallises in needles melting at 100°. The anhydrous substance melts at 144—145°. It contains one methoxyl group, has $[\alpha]_D$ − 130·4°, and occurs in the bark to the amount of 1·1 per cent. It is readily hydrolysed by dilute acids and by emulsin.

Octa-acetyl-calmatambin, $C_{19}H_{20}O_{13}(C_2H_3O)_8$, forms needles melting at 179—180°, and has $[\alpha]_D$ − 107·1°.

Calmatambetin, $C_{13}H_{18}O_8,\frac{1}{2}H_2O$, is formed together with dextrose by the action of emulsin on calmatambin according to the equation $C_{19}H_{28}O_{13} + H_2O = C_6H_{12}O_6 + C_{13}H_{18}O_8$. It crystallises in needles melting at 148—149°. It contains one methoxyl group, and is optically inactive. It is readily decomposed by the action of dilute acids, and yields a small amount of a scarlet crystalline *substance*, $C_{11}H_{12}O_3$, melting at 91°, which is volatile with steam, and has an aromatic odour; it may very possibly be a quinone.

The foregoing results show that calmatambin is a β-glucoside, having the constitution represented by the formula $CH_3{\cdot}O{\cdot}C_{12}H_{10}O_2(OH)_4{\cdot}O{\cdot}C_6H_{11}O_5$.

Calmatambin is devoid of any appreciable physiological action.

141. "*The Decomposition of Hyponitrous Acid in presence of Mineral Acids.*" By Prafulla Chandra Ray and Atul Chandra Ganguli.

Hyponitrous acid, when liberated from silver or mercurous hyponitrite by the action of dilute nitric, hydrochloric, or sulphuric acid at 25° or a higher temperature, decomposes at once according to the following equations:— (1) $2HNO = H_2O + N_2O$; (2) $5HNO = 2H_2O + HNO_3 + 4N$.

Neither nitrous acid, ammonia, or hydroxylamine is formed. The presence of the mineral acids has a specific directive influence in determining the course of reaction.

142. "*The Chemical Composition of Petroleum from Borneo.*" By Humphrey Owen Jones and Hubert Arthur Wootton.

The petroleum from Borneo has been found to consist of approximately equal quantities of homologous hydrocarbons of the paraffin, *cyclo*hexane, and aromatic series, and to contain the members of the naphthalene series to the extent of about 6 to 7 per cent. The less volatile portions of the oil are optically active.

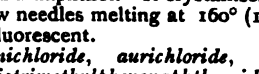
It forms a very convenient source of the nitro- and amino-derivatives of the aromatic hydrocarbons, which may be obtained in large quantities and in a highly pure state.

143. "*The Synthesis of Phenonaphthacridines: Trimethylphenonaphthacridines.*" By Alfred Senier and Percy Corlett Austin.

The authors have employed the methylene di-iodide and arylamine method (Senier and Goodwin, *Trans.*, 1902, lxxxi., 280) for the synthesis of phenonaphthacridines by using equimolecular mixtures of ψ-cumidine and naphthols, and good yields of the two desired trimethylphenonaphthacridines were obtained. When the naphthylamines were used in place of the naphthols, the product generally contained the corresponding dinaphthacridine.

The condensation of trioxymethylene with ψ-cumidine and the naphthols effected the synthesis of the same two compounds, but in this case the yields were smaller and the products less easily purified.

8 : 9 : 11-*Trimethylpheno-* *-naphthacridine*,—



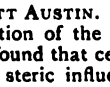
is obtained by condensation of methylene di-iodide with ψ-cumidine and α-naphthol. It crystallises from alcohol in greenish yellow needles melting at 160° (162·5° corr.); its solutions are fluorescent.

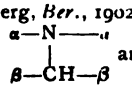
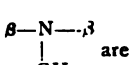
The *platinichloride*, *aurichloride*, *mercurichloride*, *picrate*, and *bistrimethylphenonaphthacridine hexabromide* were described.

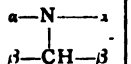
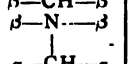
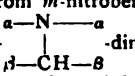
8 : 9 : 11-*Trimethylpheno-* *-naphthacridine*, isomeric with the above, was obtained in a similar manner, using β-naphthol instead of α-naphthol. It crystallises from alcohol in straw-coloured needles, melting at 136° (137° corr.), and its solutions are very faintly fluorescent.

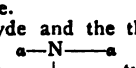
The *hydriodide*, crystallising from aniline in orange

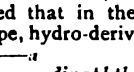
needles, appeared as an intermediate product in the preparation of the base. The *platinichloride*, *aurichloride*, and *picrate* were also described.

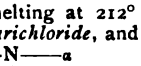
144. "*The Condensation of Aldehydes with Mixtures of α-naphthol and α-Naphthylamine: Synthesis of 7-Aryl-*  *-dinaphthacridines.*" By ALFRED SENIER and PERCY CORLETT AUSTIN.

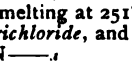
In continuation of the study of dinaphthacridines, the authors have found that certain general differences, which they ascribe to steric influence, dependent on the position of the angular rings (compare Hinsberg, *Ber.*, 1902, xxxvi., 4051) between the bases of the type  and those of the type  are well illustrated by a detailed investigation of the aldehyde, naphthol, and naphthylamine method of synthesis, first introduced by Ullmann and Fetvadjian (*Ber.*, 1903, xxxvi., 1027).

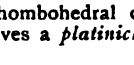
Trioxymethylene does not yield the  dinaphthacridine, whereas it readily forms the  isomeride; benzaldehyde gives the 7-phenyl derivative of both types, and from *m*-nitrobenzaldehyde was obtained 7-*m*-nitrophenyl-  -dinaphthacridine, whereas Haase (*Ber.*, 1903, xxxvi., 593) found that with β-naphthol and β-naphthylamine it gave a dihydro-derivative of the corresponding dinaphthacridine, which could not be oxidised to the base.

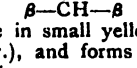
From anisaldehyde and the three tolualdehydes, only derivatives of the  -type could be obtained. It was also noticed that in the preparation of dinaphthacridines of this type, hydro-derivatives were never formed.

7-o-*Tolyl-*  *-dinaphthacridine* is obtained in yellow crystals melting at 212° (215° corr.), and forms a *platinichloride*, *aurichloride*, and *picrate*.

7-m-*Tolyl-*  *-dinaphthacridine* is a yellow crystalline powder melting at 251° (257° corr.), and gives a *platinichloride*, *aurichloride*, and *picrate*.

7-p-*Tolyl-*  *-dinaphthacridine* forms pale greenish yellow rhombohedral crystals melting at 221° (224° corr.), and gives a *platinichloride*, *aurichloride*, and *picrate*.

7-p-*Methoxyphenyl-*  *-dinaphthacridine* crystallises from benzene in small yellow rhombohedra melting at 257° (263° corr.), and forms a *platinichloride*, *aurichloride*, and *picrate*.

7-m-*Nitrophenyl-*  *-dinaphthacridine* crystallises from benzene in small yellow crystals which did not melt below 300°; no sign of fluorescence was observed in any of its solutions. The *platinichloride*, *aurichloride*, and *picrate* were prepared.

145. "*An Improved Form of Apparatus for the Rapid Estimation of Sulphates and Salts of Barium.*" By WILLIAM ROBERT LANG and THOMAS B. ALLEN.

N. Tarugi and G. Bianchi (*Gazetta*, 1906, xxxvi., [i.], 347) have described an apparatus for the rapid estimation of sulphates and salts of barium by a volumetric method based on the rapid clearing of turbid solutions in tubes of narrow calibre. Their apparatus is somewhat complicated, and the authors have simplified it materially. The solution containing the precipitated barium sulphate is forced, by air pressure applied by hand, up a narrow tube, allowed to clear—which it does rapidly as the end-point of the reaction is approached—and a drop of the precipitant added. Any milkiness is plainly observed in the narrow tube, and the solution is washed down into the flask and fresh portions forced up the tube from time to time until further addition of the reagent causes no change. Experiments were made with solutions of sulphuric acid of various concentrations, with the sulphates of copper and of nickel, and also with iron pyrites to determine its sulphur content. The errors as compared with the gravimetric estimation of sulphur as barium sulphate, range from 1 to 0·1 per cent, but such errors are materially reduced by taking the average of five or six titrations, and the whole operation can be completed in less than an hour.

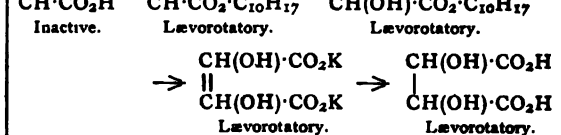
146. "*The Determination of Sugar by Fehling's Solution.*" By WILLIAM ROBERT LANG and THOMAS B. ALLEN.

The apparatus described by the authors (preceding paper) for the estimation of sulphuric acid and sulphates, based on the principle of the rapid clearing of turbid solutions in tubes of narrow calibre, was employed for the determination of dextrose by means of Fehling's solution. Accurate results were obtained when the solution was heated to its boiling-point, the concentration being not more than 0·15 grm. in 75 to 100 cc. of water, and the time of heating being five minutes. Under these conditions the average error varied from 0·1 to 0·30 per cent, but when the solutions were greatly diluted or the time of heating extended from ten to twenty minutes the results varied more than 1 per cent.

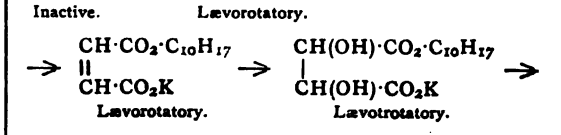
147. "*Studies in Asymmetric Synthesis.* VI. *The Asymmetric Synthesis of the Optically Active Tartaric Acids.*" By ALEXANDER MCKENZIE and HENRY WREN.

The asymmetric synthesis of *l*-tartaric acid was accomplished in three ways.

1. By the oxidation of *l*-bornyl fumarate in glacial acetic acid solution by potassium permanganate, according to the scheme:—



2. By the oxidation of the potassium salt of *l*-bornyl hydrogen fumarate in aqueous solution by potassium permanganate, thus:—



In these two cases the change $\begin{matrix}CH\cdot CO_2H\\ \|\\ CH\cdot CO_2H\end{matrix}$ (inactive) $\rightarrow$ $\begin{matrix}CH(OH)\cdot CO_2H\\ |\\ CH(OH)\cdot CO_2H\end{matrix}$ (active) is rendered possible by the introduction and subsequent complete elimination of the *l*-bornyl group.

3. By the oxidation of *l*-menthyl fumarate in an analogous manner.

The asymmetric synthesis of *d*-tartaric acid was accomplished by the oxidation of the potassium salt of *d*-bornyl hydrogen fumarate, thus :—

$$\begin{matrix}CH\cdot CO_2H\\ \|\\ CH\cdot CO_2H\\ \text{Inactive.}\end{matrix} \rightarrow \begin{matrix}CH\cdot CO_2\cdot C_{10}H_{17}\\ \|\\ CH\cdot CO_2H\\ \text{Dextrorotatory.}\end{matrix} \rightarrow \begin{matrix}CH\cdot CO_2\cdot C_{10}H_{17}\\ \|\\ CH\cdot CO_2K\\ \text{Dextrorotatory.}\end{matrix} \rightarrow \begin{matrix}CH(OH)\cdot CO_2\cdot C_{10}H_{17}\\ |\\ CH(OH)\cdot CO_2K\\ \text{Dextrorotatory.}\end{matrix} \rightarrow \begin{matrix}CH(OH)\cdot CO_2K\\ |\\ CH(OH)\cdot CO_2K\\ \text{Dextrorotatory.}\end{matrix} \rightarrow \begin{matrix}CH(OH)\cdot CO_2H\\ |\\ CH(OH)\cdot CO_2H\\ \text{Dextrorotatory.}\end{matrix}.$$

148. "*Some Derivatives of 2-Phenyl-1 : 3-naphthylenediamine.*" (Part I.). By NORMAN LEES and JOCELYN FIELD THORPE.

The β-amino-group in 2-phenyl-1 : 3-naphthylenediamine is more strongly basic than the amino-group in the α-position, and is the one first acted on in salt formation, diazotisation, and acetylation. Derivatives of the base, in the formation of which the β-amino-group takes part, can therefore be prepared directly from the base itself, whereas, since the β-amino-group can be readily protected by acetylation, those compounds which are derived from the amino-group in the α-position can be prepared from the monoacetyl derivative of the base.

2-Phenyl-1 : 3-naphthylenediamine combines with diazonium salts, forming azo-compounds, the azo-group entering in the position 4 in the naphthalene ring. The colours of these compounds do not differ appreciably in shade from those of the corresponding compounds derived from 1 : 3-naphthylenediamine; hence the presence of the phenyl group has little or no effect on the colour of compounds of this type.

Typical derivatives of the base have been prepared and investigated. The conditions have also been determined under which it is converted into the corresponding dinaphthol and the two amino-naphthols.

NOTICES OF BOOKS.

Systematic Practical Organic Chemistry. By G. M. NORMAN, B.Sc., A.R.C.Sc., F.C.S. London: University Tutorial Press, Ltd. 1907.

CANDIDATES for the Board of Education Examination in Practical Organic Chemistry, Stages I. and II., will do well to get a copy of this book, which has been written specially for them. It will be found a great convenience to have all the practical work required in one volume, so that the use of larger works can be altogether avoided, and the little book has merits which will possibly recommend it to others than those for whom it is intended. It gives clear directions for the preparation of most of the important compounds which are considered in an elementary lecture course on organic chemistry, and in most cases mentions the yield that should be obtained when the given quantities of reagents are employed. The chief reactions and properties of the substances prepared are also enumerated, and a scheme of analysis is given for the detection of any of the simple substances, either in a pure state or in aqueous solution, mentioned in the Board of Education syllabus, besides the outlines of a method of determining the class to which a substances belongs without identifying it. The book, which contains some of the recent examination papers, is well arranged, and the student who has conscientiously worked through it should have nothing to fear from his examination.

Photochemie und Beschreibung der Photographischen Chemikalien. ("Photochemistry and the Description of Photographic Chemicals"). By H. W. VOGEL. Fifth Edition. By Dr. ERNST KÖNIG. Berlin: Gustav Schmidt. 1906.

THE revision of Vogel's standard work by Dr. Ernst König, who is himself a well-known worker, more especially in the region of colour photography, has been a task of considerable magnitude, for it is sixteen years since the last edition was published. The new edition has been considerably abridged in some places, but the pages on optical sensitising, in which Vogel's important discoveries are described, have been left untouched as far as possible. This volume, which is the first part of the Handbuch der Photographie, is divided into three sections. The first gives a short account of the physical effects of light, and the second discusses at some length its chemical action, while the third and last describes the properties and uses of all kinds of photographic chemicals. Dr. König has very wisely not included methods of analysis of these chemicals, regarding such analysis as a question for chemist alone, and not coming into the province of the photographer. The work has long been known as a standard authority on all questions connected with photography, and the latest edition will be heartily welcomed by professionals and amateurs alike.

Catalogue of Bacteriological Apparatus sold by A. Gallenkamp and Co., Ltd., 19 and 21, Sun Street, Finsbury Square, London. 1907.

THIS illustrated catalogue of bacteriological apparatus includes price lists of all the ordinary apparatus required by Medical Schools, Hospitals, and Medical Officers of Health, as well as for the equipment as regards the analysis of milk, water, foods, &c., of the laboratories of Public Analysts. All kinds of sterilisers, microscopes, microtomes, polarimeters, &c., are fully illustrated, and in the cases of some of the newer or more complicated contrivances directions are given for their adjustment and use.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Berichte der Deutschen Chemischen Gesellschaft. Vol. xl., No. 9, 1907.

New Reaction to Detect Traces of Moisture.—Wilhelm Biltz.—Potassium lead iodide in contact with water is partly decomposed, yielding yellow lead iodide. To use this properly to test for the presence of water a warm solution of lead nitrate is mixed with a warm solution of potassium iodide. A yellow precipitate is first formed, and disappears on cooling, when a mass of white needles consisting of the double compound is formed. This is dissolved in acetone and filtered, and the solution can either be used as such, or else it can be precipitated with ether, and the amorphous precipitate thus obtained washed with ether and dried in a vacuum desiccator. The salt turns a

pale yellow when kept. A 20 per cent solution of the salt in acetone can be used to detect traces of moisture, a filter-paper on which it is poured turning yellow in a short time. The vapour tension corresponding to 78 per cent sulphuric acid at a temperature of 18°, which is 0·3 mm., can readily be detected. By means of a dry filter-paper impregnated with the solution the presence of water in organic liquids can be detected, or the solid substance can be used for the same purpose.

Chemical Equilibria in the Reactions between Lead Sulphide and its Oxidation Products. — Rudolf Schenck and W. Rassbach.—When the roasting process is applied to lead the following reactions are supposed to occur: $PbS + PbSO_4 = 2Pb + 2SO_2$, $PbS + 2PbO = 3Pb + SO_2$, but the conditions of these apparently simple transformations are not thoroughly understood. The authors have examined the processes to see if equilibrium ensues between the various substances formed. The components of the system are Pb, S, and O, and the possible phases Pb, PbS, $PbSO_4$, PbO (liquid or solid), and SO_2 (gaseous). In order that at any given temperature a definite SO_2 tension may be obtained which corresponds to a state of equilibrium, the presence of three solid or liquid phases is necessary. The heating of three phases to constant temperature must give a definite SO_2 reaction pressure which only depends on temperature. As four liquid or solid substances are present the following combinations are possible :— Pb, PbS, $PbSO_4$; Pb, PbS, PbO ; PbS, $PbSO_4$, PbO ; Pb, $PbSO_4$, PbO. These four combinations would correspond to the four equilibria :—

1. $PbS + PbSO_4 \rightleftarrows 2Pb + 2SO_2$.
2. $PbS + 2PbO \rightleftarrows 3Pb + SO_2$.
3. $PbS + 3PbSO_4 \rightleftarrows 4PbO + 4SO_2$.
4. $Pb + PbSO_4 \rightleftarrows 2PbO + SO_2$.

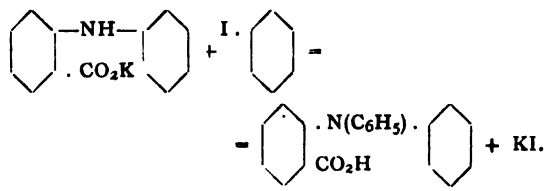
The experimental investigation of these possible equilibria shows that it is only in the first and second systems that equilibrium pressures can be observed.

Sulphation in presence of Mercury.—Otto Dimroth and W. v. Schmaedel.—A patent has recently been taken out by the Badischen Anilin und Sodafabrik for a process in which anthraquinone in sulphuric acid solution is oxidised to amino acids by nitrous acid in presence of mercury. The authors have studied the mechanism of this process, using benzoic acid in place of anthraquinone, and find that not only is the sulphation much accelerated by the presence of mercury, but also *o*-sulphobenzoic acid is produced, as well as the *m*- and *p*-compounds. Only a relatively small fraction of the benzoic acid (*i.e.*, 5 to 7·5 per cent) is sulphated in the ortho-position, and apparently two reactions occur simultaneously. In one part of the benzoic acid the hydrogen is directly replaced by the sulpho-group, giving *m*- and *p*-compounds; at the same time, the benzoic acid reacts with the mercuric sulphate, giving *o*-sulphato-mercuric benzoic acid, I—$2C_6H_4(CO_2H).Hg.SO_4H$, which with sulphuric acid regenerates mercuric sulphate and yields ortho-sulphobenzoic acid :—

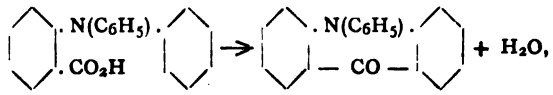
$$C_6H_4(CO_2H).Hg.SO_4H + H_2SO_4 = C_6H_4(CO_2H).SO_3H + HgSO_4 + H_2O.$$

When anthraquinone is sulphated the indirect action takes place much more quickly than the direct, and hence *a*-anthraquinone sulpho-acid is produced in excess, while the reverse is the case with benzoic acid, and therefore the ortho-compound is produced in relatively smaller quantity.

Triphenylamine and Triphenylamine Carboxylic Acid.—Irma Goldberg and Marie Nimerovsky.—Anthranilic acid can be phenylated with bromo-benzene in presence of copper, but the phenylanthranilic acid thus obtained cannot be further phenylated by the same method. If, however, iodo-benzene is used instead of the bromine compound, diphenylanthranilic acid, or triphenylamino-*o*-carboxylic acid, is readily obtained.



This method is general, and can be carried out with various derivatives of the two components. The triphenylamine-*o*-carboxylic acid thus obtained, when treated with concentrated sulphuric acid, yields N-phenyl acridon,—



and when heated above its melting-point it is converted quantitatively into triphenylamine, carbon dioxide being split off: $(C_6H_5)_2N.C_6H_4.CO_2H \rightarrow N(C_6H_5)_3$. The authors have also found that diphenylamine with iodo-benzene in presence of potassium carbonate and with copper as catalyser can be phenylated, giving pure triphenylamine :—

$$2C_6H_5.NH.C_6H_5 + 2C_6H_5I + K_2CO_3 = 2(C_6H_5)_3N + 2KI + H_2O + CO_2.$$

Phosphorus Nitride. — Alfred Stock and Hans Grüneberg.—To prepare pure phosphorus nitride the authors used phosphorus pentasulphide and ammonia. The latter they obtained in a pure dry condition by distilling it from commercial ammonia and drying by means of caustic alkali. In order to make phosphorus nitride, the ammonia need not act upon the pentasulphide in the cold, but it is sufficient if the latter is saturated with ammonia at the ordinary temperature. When the complicated mixture of ammonium thiophosphates thus prepared is heated, P_3N_5 is obtained. It is best to heat in a current of ammonia, and all the phosphorus of the original pentasulphide is readily converted into the nitride ; in fact, no other nitride can be prepared so easily in a pure state. The density of P_3N_5 at 18° is 2·51. Its colour varies from pure white to fairly dark reddish brown. The dark coloration is produced when it is heated for some time to temperatures above 850°, and the authors thought that it must be due to the presence of some free red phosphorus. However, when a dark preparation was allowed to cool quite slowly from 900° to the temperature of the room in an absolute vacuum, the colour did not disappear, although free phosphorus would certainly have evaporated. At the ordinary temperature P_3N_5 is very indifferent. It does not redden litmus-paper unless it is heated for some time with water to 100°. When warmed *in vacuo* it begins to decompose into phosphorus and nitrogen at 760°. The nitride may also be prepared in an impure state by heating a mixture of phosphorus pentasulphide and ammonium chloride, and small quantities of it remain when the reaction products of yellow phosphorus or solid phosphine with liquid ammonia are heated to a sufficiently high temperature.

Beryllium Chromate.—B. Glassmann.—To synthesise neutral beryllium chromate chromic acid was neutralised with beryllium carbonate in warm concentrated aqueous solution, and the solution thus obtained was evaporated to crystallisation. The crystals were drained from mother-liquor and dried at 100°. The chromic acid in them was then determined by precipitation as mercuric chromate from dilute nitric acid solution, and the beryllium determined in the usual way in the filtrate, after precipitation of the mercury as mercurous chloride. The formula was thus found to be $BeCrO_4.H_2O$. The reddish yellow

monoclinic crystals of $BeCrO_4.H_2O$ are completely decomposed by water, giving a yellow basic chromate. Basic beryllium chromate, which may also be prepared by precipitating a beryllium sulphate solution with ammonium chromate, is a yellow powder, insoluble in water, and having the composition $BeCrO_4.6Be(OH)_2$ when dried at 100°. The equation representing the decomposition of the neutral chromate with water is $7BeCrO_4.H_2O + 5H_2O = BeCrO_4.6Be(OH)_2 + 6H_2CrO_4$. When excess of chromic acid is added the basic salt again dissolves. The author has not succeded in preparing any acid chromates. Neutral beryllium chromate is completely analogous to magnesium chromate, dried at 100°, $MgCrO_4.H_2O$.

Thorium-cerium Mixtures.—R. J. Meyer and A. Anschütz.—An incandescent mantle of pure thorium oxide is not luminous because it is perfectly transparent to almost all wave-lengths; the addition of a coloured substance, such as cerium dioxide, produces the characteristic luminous effect. The maximum of radiation when 1 per cent of cerium dioxide is present represents the upper limit at which the increase in the power of emission caused by the increase in the amount of cerium is not appreciably affected by the disturbing influence of the ultra-red emission. Regarding the question from a chemical point of view, if such oxide mixtures are solid solutions in which the component present in excess, ThO_2, represents the solvent and the other the solute, it remains to be decided between what limits the two oxides are homogeneously miscible with one another, and whether chemical individuals are formed. These questions would easily be answered if it were possible to determine the melting-points of mixtures of different composition, which, however, is not feasible. There is also the question whether in such mixtures the cerium is actually present as dioxide and not wholly or partly as sesquioxide. To investigate this point the authors first tried to ascertain whether any oxygen escapes when ThO_2 and CeO_2 solutions are evaporated together, and obtained a negative result. However, the method employed was open to objection, and hence the active oxygen in the synthetic oxygen mixture was determined iodometrically. It was then found that only a certain part of the cerium used reacts with hydriodic acid, liberating iodine, and thus some of the cerium has been brought into the passive state, *i.e.*, some of the CeO_2 suffers a change, and loses its oxidising properties. Further experiments show that homogeneous solutions of CeO_2 in ThO_2 can be prepared up to a maximum of 7 per cent of CeO_2, but it is not certain whether this maximum percentage represents a compound of 93 per cent of ThO_2 and 7 per cent of CeO_2, which would have the formula $9ThO_2.CeO_2$. It is possible that the maximum effect is produced when 1 per cent CeO_2 is present, because the emission of light does not proceed from the whole mass of dissolved cerium, but from the dissociated parts, and that the maximum of effect corresponds to that dilution at which the solution is completely dissociated.

Products of the Action of Acetanhydride on Phthalamide.—A. Braun and J. Tcherniac.—The principal product of the reaction of acetanhydride upon phthalamide is *o*-cyanbenzamide, $C_6H_4(CO.NH_2)_2 - H_2O = C_6H_4(CN).CO.NH_2$, which is identical with Posner's *o*-cyanbenzaldoxime. When *o*-cyanbenzamide is fused (melting-point 172—173°) it passes into an isomeric substance with a higher melting-point, and the same substance is produced by the action of caustic alkali or ammonia. This isomeric compound is imidophthalamide or phthalimimide, $C_6H_4<^{CN}_{CO.(NH)H} \rightarrow C_6H_4<^{C(NH)}_{CO-\!\!-}>NH$, which gives an oxymethyl derivative with formaldehyde and a chlorimide with alkaline hypochlorite. In these reactions it is exactly analogous to phthalimide. With neutral hypochlorite the chief product of the reaction is *o*-cyanbenzoic acid.

Two New Terpenes.—Ossian Aschan.—When the liquid hydrochloride obtained by saturating raw pinene with hydrochloric acid is decomposed with bases at a high temperature and fractionated, between 145° and 150° a new terpene goes over. Its boiling-point is 145—148°, $d_{20/40} = 0.8599$; molecular refraction = 43.20; $[\alpha]_D = +1.63°$. These constants show that it is a bicyclic hydrocarbon with a double bond, and the author has given it the name pinolene. When its hydrochloride is subjected to the action of aniline another new terpene is obtained, which in its physical constants is closely allied to pinene, and which the author calls isopinene. These two terpenes are now being subjected to an exhaustive examination on a large scale. They appear to belong to the same series of bicyclic hydrocarbons as fenchene, camphene, and bornylene.

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Chem Soc

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AND

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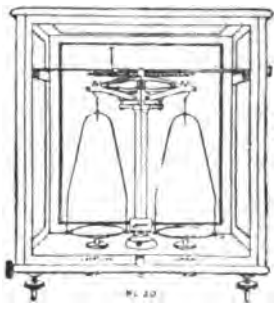

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THE CHEMICAL NEWS.

VOL. XCVI., No. 2486.

THE IGNITION POINT OF SULPHUR.

By R. H. McCREA and A. WILSON.

THE reprint of a paper by Mr. Rutherford Hill on the "Igniting Point of Sulphur" appeared in the CHEMICAL NEWS (vol. xcv., p. 169). In this paper there is a brief *résumé* of the work done on the above subject, and it appeared from it that some results had been obtained which were irreconcilable with the author's own, who had obtained the lowest point, viz., 248° C. Since then we have worked at the subject ourselves with regard to the ignition of sulphur both in air and oxygen.

We had not access to the author's previous paper in which the apparatus he used is described, so we had to evolve our own method. After various unsatisfactory results with air and paraffin baths the following method was adopted:—A small amount of sulphur—about a grm.—was placed in the bend of a U-tube of 10 mm. diameter, which was immersed in a sulphuric acid bath. One limb of this tube was connected with a water-pump, and the other, through which the aspirated air entered, was connected with a spiral of glass tubing, bent in the form of a "worm," also immersed in the sulphuric acid bath. As the question of pressure entered, a mercury manometer was connected by means of a three-way tube close to the exit limb of the U-tube. This spiral was discarded after several trials, as it did not appear to modify the results. When air was slowly aspirated through the apparatus, the manometer indicating a decrease of 2 mm. pressure, the ignition point was fairly high; but it was found by increasing the current of air till 6 mm. was registered, that the ignition point was lowered, while further increase in this direction had the reverse effect, probably through chilling. As the temperature of the sulphur naturally lagged behind that of the bath, the latter was brought slowly to the temperature required, and was maintained at this point for about five minutes, while the air was allowed to stream slowly through. When the temperature had been constant for some time the current was increased as above. It was found that for temperatures below 255° C. (uncorrected), the sulphur refused to ignite, but above this ignition easily took place. Four nearly consecutive results were obtained in this way for 255° C. (uncorrected for exposed stem).

For oxygen our results are anomalous. The following method was adopted:—Oxygen from one of Brin's cylinders was allowed to stream over the sulphur, in this case the manometer being fixed near the inlet limb. Low results were not obtained when the current of gas was passing, and the lowest results were got as follows:—Oxygen was blown through the tubes to displace the air, and was then allowed to stream through slowly while the bath was maintained at constant temperature. The current was increased for a few moments and then quickly shut off, the pressure falling to atmospheric, and ignition occurring then if the temperature was sufficiently high. The concordant results in the case of air were not obtained here, the following being the lowest:—257°, 259·5°, 259·5°, 263·5°, 264° C. (uncorrected).

As to the question of SO_2 being formed below the ignition point our results give an affirmative answer. The oxygen issuing from the apparatus was passed through a very weak solution of potassium permanganate and decolorised this; the liquid also smelt strongly of sulphur dioxide. Ten cc. of the permanganate solution were placed in a test-tube and the issuing gas (oxygen) bubbled through at the rate of one and a-half bubbles per second, at three different temperatures, under the same conditions.

At 160°	decolorisation	took	place	in 65	minutes.
At 200°	"	"	"	6·5	"
At 250°	"	"	"	3	"

(Temperatures uncorrected; permanganate about one-twentieth decinormal).

We agree with Mr. Hill that the details of apparatus may make a difference in the results obtained. We would also point out that if a thermometer is used to measure fairly high temperatures over any period it cannot be relied on. In subsequently standardising ours we found its indications in error by several degrees. We do not say that we have obtained the lowest point possible, nor do we try to explain the fact that we got a higher result with oxygen than with air. The results were undoubtedly got at a higher pressure, but the atmospheric pressure itself varies through far greater limits than this, and we have not noticed it mentioned in the other determinations. At the time of the air experiments the barometer stood at 763 mm., and in the case of oxygen at 760 mm. We would suggest that, under the conditions of the experiment, the concentration of the oxygen in the air, measured by its partial pressure, was sufficient to oxidise all the sulphur vapour formed at the temperature of ignition, measured by its vapour tension. Thus, an increase in the concentration of the oxygen—when the latter alone was used—might not lower the ignition point, the specific heat of oxygen being near that of the diluent nitrogen. In the paper referred to, Mr. Hill says that in a recent experiment "when both thermometers indicated 255° C. the sulphur vapour and air ignited," but he does not say whether this figure was read directly or corrected for the exposed part of the stem, if there were any. In the latter case the correction would make probably a considerable difference.

The temperature of ignition in air found by us, the bulb of the thermometer being placed in the bath on a level with the bend of the U-tube, and correction made for the exposed part of the stem, was 261° C.

Herne Bay, July 6th, 1907.

CONTRIBUTIONS TO THE CHEMISTRY OF GOLD.*

By F. H. CAMPBELL. M.Sc. (Melbourne).

(Concluded from p. 17).

Preparation of Aurous Oxide, Aurous Nitrate, and the Determination of the Normal Potential of Au· *Ions.*

VARIOUS methods for the preparation of Au_2O were tested. Treatment of AuCl with dilute KOH was found to be unsatisfactory, the yield being exceedingly small owing to the formation of a complex salt; further, the precipitate obtained was so fine that it was difficult to filter and purify. The precipitate obtained when insufficient $KHCO_3$ is added to a boiling solution of Au in aqua regia should be aurous hydroxide—but in practice, a mixture of Au and a substance soluble in concentrated HNO_3 was obtained. By pouring a solution of Au in aqua regia into a boiling mixture of solutions of NaOH and $Na_2C_2H_3O_2$ a small quantity of an easily washable flocculent black precipitate was obtained. With the object of increasing the yield $NaHCO_3$ was substituted for NaOH with satisfactory results; at the same time the yield was always exceedingly small, and variation in the conditions of precipitation had little or no influence. The details of the method were as follows:—The solutions were mixed when cold, and the addition of the acid solution was stopped while the

* A Paper read before the Faraday Society, May 28, 1907.

$NaHCO_3$ solution was still slightly alkaline. The resulting yellow solution became brown on warming, and at higher temperatures a flocculent light brown precipitate separated. The precipitate was filtered through a Gooch crucible, in the bottom of which was a disc of filter-paper. When free from soluble salts it was dried at 110°, separated from the paper, and treated repeatedly with cold concentrated HNO_3 in order to remove the relatively much more soluble Au_2O_3 which was always present; after a final wash with water the substance was again dried at 110°.

The brown substance so obtained was not analysed; the total amount obtained was so small and the amount required for a satisfactory analysis comparatively so large that it was considered inadvisable to use any of it in this way. That the substance was not merely metallic though containing metallic gold, as will afterwards be shown, was considered to be sufficiently proved by the facts that the colour was darker than that of gold, that it did not show metallic lustre on being rubbed with a pestle, and that it was soluble in HNO_3. In addition to the purely chemical methods of preparation an attempt was made to obtain Au_2O by anodic oxidation. A cell, having a quantity of precipitated gold as the anode and a platinum-wire as cathode, was filled with a moderately concentrated solution of K_2SO_4. A current at 10 volts was passed for some hours. At the end of the experiment it was found that, though no change had taken place at the anode, the cathode had become covered with black spongy gold. Gold was not detectable in the solution.

From the oxide the nitrate solutions were made by shaking excess of Au_2O with solutions of HNO_3 of various concentrations—the acid used was proved to be free from impurities, volatile or non-volatile. Potential measurements were made a week or longer after the solutions had been made.

On account of the smallness of the concentration of the Au_2O solubility determinations were made in the case of the two strongest only. This was done by evaporating a large bulk of the solution to dryness in a weighed porcelain dish and igniting the residue; ignition was necessary because Au_2O is not quickly decomposed at temperatures below 250°. The assumption that we have a solution of $AuNO_3$ is favoured by the fact that the residue, probably pure Au_2O, did not change its black colour for that of Au until strongly heated. It may be mentioned that a few experiments were made with a solution of H_2SO_4, and that when this was evaporated to dryness a white residue (probably Au_2SO_4) was obtained, which became first black (Au_2O) and then red (Au) on being strongly heated. In Table V. are given the results of the solubility determinations.

TABLE V.

Strength HNO_3.	No. cc. analysed.	Grms. Au found.	Grms. Au per litre.
9·13 N	150	0·0012	0·008
11·66	200	0·0032	0·016
11·66	200	0·0035	0·0175

The action between HNO_3 and Au_2O may be represented by the equation $Au_2O+2HNO_3=2AuNO_3+H_2O$ or $Au_2O+2H^{\cdot}=Au^{\cdot}+H_2O$ (see Note); hence, according to the law of mass action, $\frac{(Au_2O)\,.\,(H^{\cdot})^2}{(H_2O)\,.\,(Au^{\cdot})^2}$ = constant (see Note), the active masses of Au_2O_3 and H_2O are constant, so that the concentration of $Au^{\cdot}$ is directly proportional to that of the $H^{\cdot}$ ions; in other words, if we assume that both $AuNO_3$ and HNO_3 are equally ionised, the concentration of $AuNO_3$ varies directly, as does that of the solvent. (The table does not seem to prove this conclusion, but the error of measuring such small solubilities is too great to form a serious objection). On this assumption the concentration of $Au^{\cdot}$ ions, and hence their normal potential, that is, the potential for normality of $Au^{\cdot}$ ions, have been calculated in the case of those solutions in which no direct concentration estimation was possible (compare Cumming, *Trans. Faraday Soc.*, Feb., 1907, ii., 205).

(NOTE.—This equation contains even the action of any other acid in aqueous solution on aurous oxide, and explains why aurous fluoride cannot exist, the hydrofluoric acid forming very little $H^{\cdot}$ ions; see Lenher, *Journ. Am. Chem. Soc.*, 1903, xxv., 1136).

The potential measurements were made by means of the compensation method; a sensitive d'Arsonval galvanometer served as Nul instrument. As it was found impossible to obtain satisfactory measurements unless the electrode was in contact with solid Au_2O, a slight modification was made in the ordinary form of electrode vessel; a tube about 2 mm. in length and 1 mm. in diameter was sealed to the bottom of the cell. By these means the short wire electrode could be completely covered by a very small quantity of the solid. The electrodes consisted of platinum-wires, sealed into glass tubes in such a way that about 2 mm. of the wire was left exposed; connection was made by means of a copper-wire joined to the protected end of the platinum. It was found that platinised platinum and gilded electrodes gave the same results, and that these agreed with those obtained when a platinum electrode was used in contact with a mixture of pure Au and Au_2O, prepared as already described. This would serve to show that the Au_2O used has an admixture of metallic gold, which forms the lower oxidation state of the reversible Au_2O electrode. Most of the measurements were made with platinised platinum electrodes.

In Table VI are given the potentials measured, ϵ, and the normal potential, ϵ_0, calculated from them by means of Nernst's formula:—$\epsilon=\epsilon_0+\frac{RT}{n\mathrm{F}}\log_n i$. In the case under consideration the valency $n=1$, so that $\epsilon_0=\epsilon_1-0{\cdot}059\log_{10} i$; i being the concentration of the mols. gold in solution taken as being $Au^{\cdot}$ ions.

TABLE VI.

HNO_3 normality.	Grm.-mols. of Au^1 per litre.	ϵ against n calomel electrode.	ϵ against n hydrogen electrode.	ϵ_0
3·32	0·00002 (*a*)	0·835	1·118	1·40
7·76	0·000047 (*a*)	0·901	1·184	1·44
8·77	0·000053 (*a*)	0·923	1·206	1·46
9·13	0·000041	0·932	1·215	1·47
11·66	0·000086	0·998	1·281	1·52
			Mean =	1·46

(*a*) These values were obtained by interpolation from the solubility values given in Table V., on the assumption that $(Au^1)=0{\cdot}6\ 10{-}5\ (HNO_3)$, as calculated from the average solubility product $0{\cdot}7\ 10{-}19$ of AuOH. This approximation is probably sufficiently accurate for present purposes, as any variation in the value for Au^1 makes a comparatively small alteration in ϵ_0.

A normal calomel electrode was used as the other half-cell, and the two connected by means of a saturated ammonium nitrate solution, to eliminate, as far as possible, the diffusion potential (Cumming, *Trans. Faraday Soc.*, 1907, ii., 213). The above figures ϵ_0 represent the normal potential of $Au^{\cdot}$ ions compared with the hydrogen standard. Taking the mean, we have as limiting minimum value for the normal potential, $\epsilon_h Au_{metal}/1nAu^{\cdot}=+1{\cdot}5$ volts above hydrogen standard. The value 1·5 of the $Au^{\cdot}$ potential being considerably above that of oxygen, 1·22, the fact that the aurous compound is very labile and difficult to prepare are easily explicable. In fact, according to these figures the dissociation tension of O_2 from Au_2O is far greater than the atmosphere. From the hydrolysis of $AuNO_3$, *i.e.*, the solubility of Au_2O in HNO_3, we are able to calculate the approximate value of the solubility product $(Au^{\cdot})\,(OH')$ of Au_2O. $(Au^{\cdot})\,(OH')=(Au^{\cdot})\,\frac{1{\cdot}2\times10{-}14}{(H^{\cdot})}$ assuming $(Au^{\cdot})$ to be the concentration of Au dissolved and $(H^{\cdot})$ that of the HNO_3. Hence we get—

Table VII.

Strength of acid.	Solubility product.
9·13 *n*	$0·52 \times 10^{-19}$
11·66	$0·86 \times 10^{-19}$

The small affinity between gold and iodine, the tendency to form an iodine complex, the high oxidation potential of Au· ions, and the very low solubility product of Au_2O all agree to confirm the assumption that Au forms very weak positive ions.

With respect to the trivalent state, the results show that the same is true. The tendency of aurous compounds to decompose into an auric compound and metallic gold probably indicates that an equilibrium between the two states exists in which the concentration of each is of the same order of magnitude, and hence of approximately the same potential against the metal.

I take this opportunity to express my deepest thanks to Prof. Abegg, by whom the subject of this research was suggested, and to whose continual interest and advice its success is largely due.

RETIREMENT OF PROFESSOR LUNGE.

The news of the approaching retirement of Dr. Georg Lunge from the professorship of Technical Chemistry at Zurich Polytechnic will be received with great regret by all who know of his valuable work as a teacher, in a post which he has held for more than thirty years. His loss will be felt keenly by his students, for to them he has been not only a lecturer whose knowledge of technical chemistry is unequalled, but also a personal friend, who was ever ready to place at their disposal his experience and counsel. Professor Lunge has an extensive circle of friends in England, for he spent some years in this country while acting as manager of large soda works in the Tyne district, a post he gave up only when appointed to the Professorship at Zurich. His "Text Book of the Soda Industry," the first volume of which appeared in 1879, is still the standard book upon the subject, while his "Treatise on the Chemical Examination of Technical Products" is one of the most comprehensive works on analysis extant. His investigations of the lead chamber reactions in the manufacture of sulphuric acid and upon the composition and action of bleaching-powder early made his name known all over Europe as a worker of great skill and ingenuity, while the wideness of his knowledge of technical chemistry may be gauged by calling to mind the text-books upon different branches of technology which came from his pen. It only remains for us to express the hope that he may live many years to enjoy the rest from his arduous professional duties, which latterly imposed too great a strain upon both mind and body, and that he may have sufficient strength to add to the number of valuable books which he has already given to the world.

Alloys of Nickel and Tin.—Em. Vigouroux.—Alloys of nickel and tin, containing from 0 to 40 per cent of the latter, may be prepared by heating a mixture of the two metals in a current of hydrogen in a Schlœsing furnace. Such alloys are feebly magnetic, and yield, when treated with nitric acid and potash, a substance with the formula Ni_3Sn. This substance when powdered is brown in colour; it is non-magnetic and is soluble in nickel. Its density at 0° is 8·98. It is attacked by oxygen at a red heat and by chlorine. Hydrochloric acid acts upon it at ordinary temperatures even when dilute, and completely dissolves it when heated. Sulphuric acid acts more rapidly, and aqua regia more energetically still. Cold dilute nitric acid has but little action, but the hot concentrated acid gives metastannic acid. Potash solution has no action upon it, and fused potash corrodes it only very slowly. — *Comptes Rendus*, cxliv., No. 24.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, July 4th, 1907.

Sir Alexander Pedler, C.I.E., F.R.S., Vice-President, in the Chair.

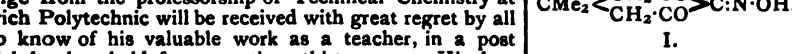
Messrs. M. D. Cowap, H. McCombie, O. E. Elias, and S. F. Stell were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Benjamin Owen Jones, Boksburg, Transvaal; Thomas Callan, B.Sc., 22, Church Street, Egremont, Cheshire; Robert Harry Smith, Apsley House, Priory Road, Sheffield.

Of the following papers, those marked * were read:—

*149. "iso*Nitroso- and Nitro-dimethyldihydroresorcin.*" By Paul Haas.

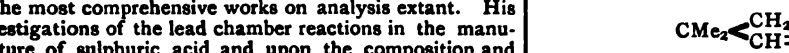
When an ice-cold aqueous solution of the potassium salt of dimethyldihydroresorcin mixed with potassium nitrite is acidified, a pale yellow precipitate of iso*nitrosodimethyldihydroresorcin* (I.)—



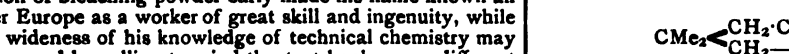
I. II.

is obtained. That this substance is in reality an *iso*nitroso-derivative and not a nitroso-derivative is shown by the fact that it does not give Liebermann's reaction, but on the contrary yields coloured *potassium*, *ammonium*, and *ferrous* salts after the manner of α-oximino-ketones. When *iso*nitrosodimethyldihydroresorcin suspended in ether is saturated with oxides of nitrogen, prepared from nitric acid and arsenious oxide, it is converted into *nitrodimethyldihydroresorcin* (II.); this substance may also be prepared in a similar manner from dimethyldihydroresorcin itself.

The base (III.), obtained by the action of ammonia on dimethyldihydroresorcin (*Trans.*, 1906, lxxxix., 191)—

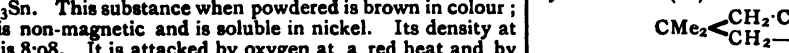


III.



IV.

when suspended in water and treated with nitrous acid at 0°, yields an iso*nitroso*-derivative of the formula (IV.), which gives a crimson *potassium* salt and a blue *ferrous* salt. Both *iso*nitroso- (I.) and nitro-dimethyldihydroresorcin (II.) on reduction yield an amine which is converted by nitrous acid into a substance of the formula $C_8H_{10}O_2N_2$. That nitrous acid in acting on the base (III.) really attacks the carbon atom in the para-position relative to the two methyl groups, and not the imino-group, is shown by the fact that this *iso*nitroso-derivative (IV.) yields on reduction and subsequent treatment with nitrous acid, the same substance, $C_8H_{11}ON_3$, as is obtained by a similar series of reactions from the *mono-oxime* of *iso*nitrosodimethyldihydroresorcin (V.)—



V.

in which the nitrogen atoms are clearly attached to different carbon atoms.

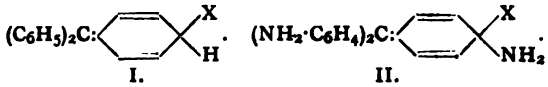
*150. "*The Structure of Carbonium Salts.*" By Frank Baker.

The author has examined the absorption spectra of the sulphates of several derivatives of benzylideneacetone, and

also of triphenyl- and trianisyl-carbinol sulphates. These carbonium salts gave rise to two characteristic types of absorption.

p-Rosaniline base, as well as the mono-hydrochloride, shows the first type of curve, whilst in presence of more concentrated acid the second of these types of spectra is observed. From these results, the author concluded that the magentas are carbonium salts, similar to triphenyl-carbinol sulphate.

Since Gomberg (*Ber.*, 1907, xl., 1847) has shown that the latter compound possesses the structure I., the constitution II. was ascribed by the author to the salts of *p*-rosaniline with one equivalent of acid.



I. II.

The second of the above-mentioned types of curve is similar to those of the hydrochlorides of certain members of the hydroxyazo-group (Tuck, *Trans.*, 1907, xci., 449), and the author suggested that these salts are also carbonium compounds.

The absorption spectrum of triphenylmethane was found to differ from that previously described by Hartley (*Trans.*, 1887, li., 152).

DISCUSSION.

Dr. CAIN mentioned that Gomberg himself, in the paper quoted by the author, adopted Nietzki's formula, $(NH_2 \cdot C_6H_4)_2C{:}\langle{=}\rangle NH_2X$, for the salts of *p*-rosaniline. In view of the work of Hantzsch and Ostwald, and other chemists, which are generally considered to establish the correctness of Nietzki's formula, it was not likely that Mr. Baker's suggestion would be accepted by colour chemists, particularly as it seemed so improbable that the acidic group X should be attached to the carbon and not to the nitrogen atom.

Dr. HEWITT saw no necessity to ascribe a carbonium formula to the salts of hydroxyazo-compounds with mineral acids. Chemical reactions pointed to their substances having a quinonoid structure, but it was the phenolic nucleus which apparently becomes altered.

In reply, Mr. BAKER pointed out that Gomberg had suggested that in the formation of magenta from *p*-rosaniline base a carbinol corresponding to the salt of the structure shown by (II.) was first formed, and that this compound passed into the iminoquinone, but no proof of the latter change had been presented.

*151. "*Studies of Dynamic Isomerism.* Part VI. *The Influence of Impurities on the Mutarotation of Nitrocamphor.*" By THOMAS MARTIN LOWRY and EGBERT HOCHEY MAGSON.

The velocity of mutarotation of nitrocamphor has been measured in a number of different solvents and in presence of a variety of added impurities.

In the experiments on glucose described in the first paper of this series (*Trans.*, 1903, lxxxiii., 1314), it was found that the mutarotation in aqueous solutions could not be retarded by the addition of either acid or alkali, and appeared to be due to a direct interaction between the sugar and the solvent. In the case of nitrocamphor dissolved in chloroform, however, it has been found possible to retard the isomeric change by the addition of small quantities of acid, thus confirming the view already arrived at (*Trans.*, 1899, lxxv., 221) that the mutarotation of the nitrocamphor in solvents such as chloroform and benzene is conditioned by the presence of alkaline impurities.

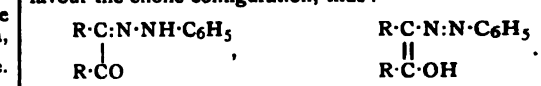
Sodium ethoxide added to an alcoholic solution of nitrocamphor was found to produce an acceleration very similar to that which results from the addition of potassium hydroxide to an aqueous solution of glucose. Extraordinary effects were produced, however, by the addition of piperidine to solutions of nitrocamphor in benzene or chloroform. In presence of N/1000 piperidine no mutarotation could be detected, with N/10,000 piperidine the mutarotation was complete in five minutes, with N/100,000 in an hour, and with N/1,000,000 in about ten hours; with N/10,000,000 piperidine the acceleration was of the same order of magnitude as that due to the trace of impurity normally present in the purified materials.

DISCUSSION.

Mr. W. A. DAVIS, replying to the question raised by Dr. Lowry as to the origin of the peculiar odour noticed in the chloroform solutions used, suggested that it was due to carbonyl chloride formed by the action of the air on the chloroform. It would appear that this change was accelerated by the presence of an acid, in this case trichloroacetic acid; it was already well known that it could be prevented by having an alkali present, such as lime.

*152. "*The Relation between Absorption Spectra and Chemical Constitution.* Part VIII. *The Phenylhydrazones and Osazones of α-Diketones.*" By EDWARD CHARLES CYRIL BALY, WILLIAM BRADSHAW TUCK, EFFIE GWENDOLINE MARSDEN, and (in part) MAUD GAZDAR.

From a consideration of their absorption spectra it was shown that the phenylhydrazones and osazones of the α-diketones in neutral solution possess the ketonic constitution, and that in alkaline solution the former tend to favour the enolic configuration, thus:—



Neutral solution. Alkaline solution.

In the phenylhydrazones of hydroxy-ketones in which the hydroxyl group is adjacent to the :C:N· linking, direct evidence is found of the mutual influence of the hydroxyl group and the C:N linking. This influence is best shown in the great retardation of the change of the hydrazone to the azo-form in light; moreover, it is this mutual influence which renders possible the oxidation of the hydroxyl group by excess of phenylhydrazine. Inasmuch as the change to the azo-form removes this influence upon the hydroxyl group, this change tends to restrain the oxidation of the hydroxyl group by phenylhydrazine, and as, further, acetic acid retards the change to the azo-form, so the presence of acetic acid aids the formation of the osazones with excess of phenylhydrazine.

153. "*Permanganic Acid.*" By MATTHEW MONCRIEFF PATTISON MUIR.

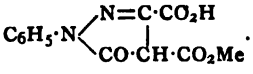
By adding the equivalent quantity of dilute sulphuric acid to a solution of barium permanganate, filtering through glass-wool, and evaporating over sulphuric acid in a vacuum, solutions of permanganic acid, $HMnO_4$, containing about 17 per cent of the acid, can be obtained. A small quantity of a fairly concentrated solution of this acid, when left in an open vessel, deposits brown oxides of manganese ($xMnO_2$, $yMnO$, where $x = 20$ and y varies from 6 to 10), mixed with violet-blue crystals of the acid. The latter could not be obtained as a solid except mixed with oxides of manganese. A very dilute solution of permanganic acid can be boiled without decomposition; a solution containing about 4 per cent of the acid deposits a brown film on glass on keeping for half-an-hour. More concentrated solutions decompose gradually with evolution of ozonised oxygen; when evaporated to dryness over sulphuric acid in a vacuum, they give black, almost pure, manganese dioxide.

154. "*Methyl Dicarboxyaconitate.*" By SIEGFRIED RUHEMANN.

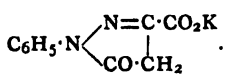
The author has found that the esters of dicarboxyaconitic acid are not produced in a manner similar to the formation of ethyl dicarboxyglutaconate, namely, by the action of the esters of trichloroacetic acid on ethyl sodiomalonate, but methyl dicarboxyaconitate

$CO_2Me{\cdot}C{:}C(CO_2Me)_2{\cdot}CH(CO_2Me)_2$, was prepared according to the directions of Anschütz and Deschaur (*Annalen*, 1906, cccxlvii., 3).

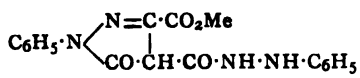
Phenylhydrazine reacts with the ester at the ordinary temperature to yield the *additive* product, $CO_2Me{\cdot}C(NH{\cdot}NH{\cdot}C_6H_5)[CH(CO_2Me)_2]_2$ (colourless prisms, m. p. 135°). This is fairly stable, but is decomposed when it is digested with dilute caustic potash or boiled with sodium carbonate with formation of malonic acid and *monomethyl phenylpyrazolonedicarboxylate* (colourless prisms which melt and decompose at 201—202°). The author considers that the formula of this ester is—



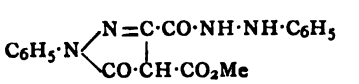
On boiling with concentrated aqueous potassium hydroxide, it furnishes potassium 1-phenyl-5-pyrazolone-3-carboxylate,—



At 100°, phenylhydrazine and methyl dicarboxyaconitate form, besides methyl malonate, the compound $C_{24}H_{24}O_4N_6$. This, with dilute hydrochloric acid, yields phenylhydrazine hydrochloride and the *phenylhydrazide* of *monomethyl phenylpyrazolonedicarboxylate*,—



or—



(colourless needles which decompose on heating).

The compound $C_{24}H_{24}O_4N_6$ therefore is the *phenylhydrazine* salt of this substance.

Methyl dicarboxyaconitate, on being heated with aniline at 100°, is decomposed, and furnishes *carboxymethylanilinomethylenemalonanil*,—

$$CO_2Me{\cdot}C(NH{\cdot}C_6H_5){:}C{<}\begin{matrix}CO\\CO\end{matrix}{>}N{\cdot}C_6H_5$$

(canary-yellow prisms, m. p. 194°).

155. "*The Action of Heat on α-Hydroxycarboxylic Acids.* Part III. *αα'-Dihydroxysebacic Acid and its Diacetyl Derivative.*" By HENRY RONDEL LE SUEUR.

The author has now extended his investigation of the action of heat on α-hydroxy-acids to the hydroxy-derivatives of dibasic acids. When αα'-dihydroxysebacic acid or its diacetyl derivative is heated at 250—270°, it decomposes with evolution of carbon monoxide and formation of the dialdehyde of suberic acid :—

$$CO_2H{\cdot}CH(OH){\cdot}[CH_2]_6{\cdot}CH(OH){\cdot}CO_2H \rightarrow CHO{\cdot}[CH_2]_6{\cdot}CHO.$$

156. "*Dihydroxyadipic Acids.*" (Preliminary Note). By HENRY RONDEL LE SUEUR.

When the bromine atoms in αα'-dibromoadipic acid are replaced by hydroxyl groups, two dihydroxyadipic acids are obtained, one melting at 146° and the other at 174°. Both form insoluble crystalline silver salts, and when the acid melting at 146° is heated, it loses water, with formation of a dilactone which sublimes in well-defined plates.

As αα'-dihydroxyadipic acid contains two asymmetric carbon atoms, it is probable that the above acids are stereoisomerides.

157. "*The Relation between Absorption Spectra and Optical Rotatory Power.* Part II. *The Tartaric Acids.*" By ALFRED WALTER STEWART.

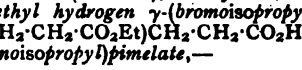
The absorption spectra of the two active forms of tartaric acid are identical, and show only slight general absorption. When an equimolecular mixture of the two antipodes containing the same weight of acid as in the previous cases is used, a greater general absorption is found, proving that racemic acid has a greater power of absorption than either active form. When the racemic acid solution is diluted, however, its absorptive power gradually approximates to that of the active acids, with which it eventually becomes identical. This shows that in dilute solution the racemic acid is broken down into the two active forms, as has already been suspected from results obtained in freezing-point, boiling-point, and vapour density determinations. These spectroscopic results were corroborated by somewhat similar ones obtained with the active limonenes and dipentene. As a double salt above and below its temperature of transition furnishes the closest parallel to a solution which may contain either a mixture of two antipodes or a racemic compound, the spectrum of astrakanite above and below 22° was examined. It was found that above this temperature an absorptive power was shown differing from that observed below 22°, so that the two cases are evidently analogous. This also furnishes a new method of determining transition temperatures. It was found that *i*-tartaric acid had the strongest absorptive power of all, being much more absorbent than racemic acid. No absorption bands were found in any of the spectra. Applications of this work to various questions, such as the determination of existence limits in the case of racemic compounds, the proof of the actual formation of a liquid racemic compound (as distinct from an inactive equimolecular mixture), and the existence of pseudo-racemic compounds were discussed.

158. "*Experiments on the Synthesis of the Terpenes.* Part XI. *Synthesis of* 4-Iso*propylidene*cyclo*hexanone and its Derivatives.*" By WILLIAM HENRY PERKIN, jun., and JOHN LIONEL SIMONSEN.

The sodium derivative of ethyl α-acetylglutarate, $CO_2Et{\cdot}CHNa(COMe)CH_2{\cdot}CH_2{\cdot}CO_2Et$, reacts readily with ethyl β-iodopropionate with the formation of *ethyl γ-acetylpentane-αγε-tricarboxylate*,—

$$CO_2Et{\cdot}C(COMe)(CH_2{\cdot}CH_2{\cdot}CO_2Et)_2,$$

which distils at 217° (15 mm.), and on hydrolysis with hydrochloric acid is converted into *γ.acetylpimelic acid*, $COMe{\cdot}CH(CH_2{\cdot}CH_2{\cdot}CO_2H)_2$. This acid is a colourless syrup which yields a *semicarbazone* melting at 177°. When ethyl γ-acetylpimelate is treated with magnesium methyl iodide, it is converted into the lactone of *ethyl hydrogen* γ-iso*propenolpimelate*,—

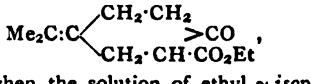


which distils at 200° (22 mm.), and yields, with hydrobromic acid, *ethyl hydrogen γ-(bromoisopropyl)pimelate*, $Me_2CBr{\cdot}CH(CH_2{\cdot}CH_2{\cdot}CO_2Et)CH_2{\cdot}CH_2{\cdot}CO_2H$.

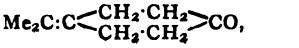
Ethyl γ-(bromoisopropyl)pimelate,—

$$Me_2CBr{\cdot}CH(CH_2{\cdot}CH_2{\cdot}CO_2Et)_2,$$

obtained by the esterification of the latter compound, is decomposed by pyridine with formation of *ethyl γ-isopropylidenepimelate*, $Me_2C{:}C(CH_2{\cdot}CH_2{\cdot}CO_2Et)_2$ (b. p. 168° under 13 mm.), and on hydrolysis, yields *γ-isopropylidenepimelic acid*, which crystallises in prisms and melts at 97°. *Ethyl* 4-iso*propylidene*cyclo*hexanone-2-carboxylate*,—



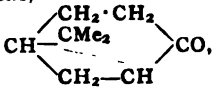
is obtained when the solution of ethyl *γ-iso*propylidenepimelate in toluene is treated with sodium; it decomposes on distillation, combines with hydrogen bromide to form *ethyl-4-β-bromoisopropylcyclohexanone-2-carboxylate*, and is hydrolysed by alcoholic potash with formation of 4-iso*propylidene*cyclo*hexanone*,—



This ketone distils at 219°—221°, and yields a *semicarbazone* which melts at 201°; hydrobromic acid converts it into 4-*β-bromo*isopropylcyclo*hexanone*,—

$$Me_2CBr\cdot CH\begin{<}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{>}CO.$$

The object of this research was to endeavour to synthesise nopinone,—



from the above bromo-ketone by the elimination of hydrogen bromide, but the experiments which were made in this direction have so far been unsuccessful.

159. "*The Purification of Acetic Ester.*" By John Kenneth Harold Inglis and Lottie Emily Knight.

Great difficulty has always been experienced in preparing pure acetic ester, and although several methods have been suggested, no one of them is satisfactory, since the yield of pure ester is small, and the process of preparing it laborious. For the preparation of aceto-acetic ester, very nearly pure acetic ester is required, and the presence of a moderate quantity of alcohol—the most likely impurity—is fatal to success. A series of experiments has shown that the separation can be most easily carried out by first converting the alcohoh nto an ester of high boiling-point, and then distilling. If the crude ester, as obtained in the ordinary continuous process, is dried over potassium carbonate (which also removes any acetic acid) and treated with phosphoric oxide, a slow action takes place with the formation of phosphoric esters which are neither volatile nor decomposed at the boiling-point of ethyl acetate (77·20° corr.). In this way a yield of 160 grms. of ester boiling within one degree was obtained in an experiment in which the theoretical yield was 264 grms.; that is 60 per cent of ester was obtained pure.

This process, however, is slow, and requires several days for completion at the ordinary temperature. On the other hand, the removal of the alcohol takes place more rapidly at the boiling-point. Thus, a mixture of 100 grms. of ester (b. p. 76·65—77·15°) with 8 grms. of absolute alcohol distilled continuously between 73° and 77°, only 21 grms. passing over above 76·3°. When, however, the fractions had been mixed together and heated for half-an-hour with 10 grms. of phosphoric oxide, using a reflux condenser, a single distillation gave 72 grms. of distillate between 76·7° and 77·2°; that is, 72 per cent of an approximately pure substance. This result shows that it is easy to obtain by this method a good yield of acetic ester boiling within.0·5°; and it was found that an ester of this purity gave a good yield of acetoacetic ester.

160. "*Solubility of Lead Sulphate in Concentrated Solutions of Ammonium Acetate.*" (Preliminary Note). By John Jacob Fox.

Solubility experiments were carried out with the view of determining the course of the reaction occurring between ammonium acetate and lead sulphate. The solid phases were examined to ascertain whether they changed during the solution. The following are some of the results obtained from the analysis of the solutions saturated at 24·9°, the concentration of the ammonium acetate varying from about normal upwards:—

Density of solution	Molecules of salt per 1000 molecules of water— Ammonium acetate.	Ammonium sulphate	Lead acetate.
1·0197	20·0	0·54	0·52
1·0320	31·2	0·93	0·92
1·0457	44·5	1·49	1·46
1·0578	55·6	2·11	2·08
1·0694	68·5	2·77	2·74
1·1094	94·1	2·77	6·31
1·1281	133·3	2·80	8·10

The curve obtained does not agree with the formula developed by Noyes (*Amer. Chem. Soc.*, 1905, xxvii., 747), the solubility being greater than that given by the formula. The solid phase consisted of lead sulphate and was unaltered with concentrations of ammonium acetate up to rather more than 3N, but with more concentrated ammonium acetate, well-defined crystals of lead ammonium sulphate, $Pb(NH_4)_2(SO_4)_2$, were obtained.

The solubility of the lead sulphate increased considerably with ammonium acetate of greater concentrations than above, and the solid phases consisted of mixtures of lead sulphate and lead ammonium sulphate. The lead is probably present in solution as lead acetate, since the amount of sulphate in solution gradually became less than the equivalent of the lead present as the concentration of the ammonium acetate was increased beyond 3N.

161. "*Researches on Morphine.*" (Part III.) By Frederic Herbert Lees.

In continuation of previous work (Schryver and Lees, *Trans.*, 1900, lxxvii., 1024; 1901, lxxix., 563; and Lees and Tutin, *Proc.*, 1906, xxii., 253), the author has shown that chloromorphide and bromomorphide yield chlorocodeide and bromocodeide respectively on methylation, the two latter bases previously obtained by other methods being simply the codeine analogues of the two former bases.

By the hydrolysis of chloromorphide, the author has isolated, besides *β-iso*morphine, an hitherto undescribed isomeride of morphine previously indicated by the hydrochloride ($[\alpha]_D$ −92·5°) obtained by Schryver and Lees. On methylation, this new base gives the so-called "*ψ*-codeine" (compare Merck, *Arch. Pharm.*, 1891, ccxxix., 161; Vongerichten, *Ber.*, 1903, xxxvi., 1591, and Knorr and Hörlein, *Ber.*, 1906, xxxix., 4409).

As the name *ψ*-morphine belongs to a well known oxidation product of morphine of which Merck's "*ψ*-codeine" is not the methyl ether or codeine analogue, the author has termed the new isomeride of morphine, *neo*iso*morphine* and its methyl ether, *neoisocodeine*

Neoisomorphine, $C_{17}H_{19}O_3N$, crystallises from alcohol in brilliant, prismatic needles containing one molecule of the solvent (m. p. 278°); its *hydrochloride*, $C_{17}H_{19}O_3N,HCl$, forms anhydrous crystals from alcohol ($[\alpha]_D$ −79·1° in water;) its *methiodide*, $C_{17}H_{19}O_3N,MeI$, forms glistening crystals from alcohol (m. p. 297°; $[\alpha_D$ −54·5° in water).

Neoisocodeine, $C_{18}H_{21}O_3N$, forms large colourless prisms from ethyl acetate (m. p. 181—182°; $[\alpha']_D$ 96·6° in alcohol).

*β-iso*Morphine on methylation furnishes *β-isocodeine*, $C_{18}H_{21}O_3N$, which did not crystallise. The *methiodide*, $C_{18}H_{21}O_3N,MeI$, forms tabular crystals from water (m. p. 215—216°; $[\alpha]_D$ −145·5° in water), and on boiling with sodium hydroxide readily yields a methine base.

It was also shown that the "*A-Base*" (m. p. 147—147·5°; $[\alpha]_D$ −205·5° in chloroform) previously obtained by Lees and Tutin (*loc. cit.*) together with *iso*codeine (m. p. 171—172°; $[\alpha]_D$ −155° in chloroform) by the hydrolysis of bromocodeide as a definite substance, not resolvable by re-crystallisation, is in reality a molecular combination of *iso*codeine and *β-iso*codeine.

PHYSICAL SOCIETY.

Ordinary Meeting, June 28th, 1907.

Prof. W. E. Ayrton, Past-President, in the Chair.

Mr. J. T. Irwin gave a demonstration of the uses of his Hot-wire Oscillographs and Hot-wire Wattmeters.

After giving an explanation of the principle of the hot-wire oscillograph, and pointing out how to obtain exact compensation for the heat capacity of the wires by means of electric capacity or self-induction, Mr. Irwin showed the following experiments with the oscillograph:—

1. The P.D. from a rotary converter (*a*) with the ripples due to sparking damped out by resistance in the condenser-circuit, (*b*) with the ripples shown at their proper size with critical damping, (*c*) with the ripples very much exaggerated owing to want of damping.

2. The periodic discharge of a condenser through a self-induction (*a*) with a small resistance in circuit and therefore an oscillatory discharge, (*b*) with a large resistance in circuit and the oscillations damped out.

3. The P.D. across the stator of an induction-motor and the current in the rotor below, above, and at synchronous speed, (*a*) as a two-phase machine, (*b*) as a single-phase machine.

4. The current through and the P.D. across the armature of a single-phase commutating compensated motor run up to and above synchronous speed, (*a*) with the auxiliary brushes short-circuited showing the current and P.D. in phase with each other at synchronous speed, (*b*) with the auxiliary brushes open-circuited showing the P.D. and current differing by nearly 90° in phase.

5. A circle and a straight line produced by combining, by means of a beam of light, the vertical harmonic motion of a mirror with the simple harmonic motion of the oscillo graph due to a sine wave of current, the circle being produced when the two movements were at 90° difference in phase, and the straight line when the two movements were in phase.

6. A hysteresis-loop for glass-hard steel wire, showing the rounding-off of the tips at a frequency of 40 per second.

Mr. Irwin also showed a new type of synchronous motor which he has invented and which can be run easily at synchronous or half-synchronous speed. This motor consists essentially of a series motor with laminated fields and with two points on the commutator 180 electrical degrees apart shorted.

A hot-wire instrument to measure mean watts was also shown.

Mr. W. DUDDELL expressed his interest in the fact that Mr. Irwin had succeeded in designing an oscillograph depending for its action on thermal effects. Referring to the hysteresis loops shown by the author, he said it was important to know the form of these loops in actual work. He was doubtful, however, whether the blunted points were due to hysteresis effects or whether they were due to instrumental defects.

Mr. A. RUSSELL congratulated the author on his extremely novel and interesting instruments. Apart from the practical utility of the invention, which the experiments shown amply demonstrated, there were many points in connection with the working of the instrument which elucidated physical laws. For instance, in his paper to the Institution of Electrical Engineers, Mr. Irwin gave figures from which it could be deduced that Newton's law of cooling was very approximately true for the wire strips of his instrument slowly cooling in air. The practical working of his oscillograph proved that Newton's law of cooling was also very approximately true even when the periodic time of the temperature fluctuation of the strips was only a very small fraction of a second—a physical result of considerable importance.

Mr. J. S. Dow described a form of Photometer in which the cosine law was utilised. It was therefore unnecessary to move either the photometer or the sources of light. The adjustment of the illumination of the photometrical surfaces was carried out in the photometer itself by the rotation of a Ritchie wedge about the boundary-line between the photometrical surfaces as axis. The ratio of the candle-powers of the two sources of light compared could then be read off on a suitably calibrated scale attached to the photometer.

This type of instrument is very convenient. Attention was drawn, however. to the possibility of "angle errors" and the means of avoiding them.

This instrument could be used on the equality of brightness principle, or, by utilising an oscillating lens, as a flicker photometer. The results of using these two photometrical methods were, in this case, in very good agreement. Yet this might not have been the case if a different portion of the retina had been utilised, especially at low illuminations.

An experiment was then shown illustrating the behaviour of the "rods" and "cones" as regards flicker. At strong illuminations, when the cones are predominant, the perception of form and colour is most acute when the central portion of the retina is utilised; but at low illuminations, when the rods are in action, visual acuteness is best when the outer region of the retina is used.

In the same way the perception of flicker was demonstrated to be only most acute over the portion of the retina removed from the centre of the eye when a weak illumination is employed. A distinction must be drawn between "rod-flicker" and "cone-flicker."

Some experiments were then shown illustrating the detail-revealing powers of red and green light. A green or blue surface loses in luminosity as the image of it fades more and more towards the centre of the retina. But apart from the question of luminosity, the red end of the spectrum gives the best definition in the case of distant vision and the blue end in the case of very close vision. This arises from the want of achromatism of the eye.

Two exactly similar patches of red and blue light were thrown upon a screen on which a black and white chessboard pattern had been traced. The black and white squares were then seen to be more sharply defined when illuminated by the red light, in spite of the fact that the illumination due to the blue light was much the brighter of the two. The red end of the spectrum is therefore, in general, the most effectual portion for the illumination of clocks, shop-signs, and objects which must be viewed from a distance.

Mr. PATTERSON complimented the author upon his paper and experiments. With reference to the cosine instrument he asked if the cosine law was trustworthy at very acute incidence of the light. The unequal sensitiveness of different parts of the retina accounted for the fact that it was possible to obtain different balance-points by fixing attention on the different sides of a Ritchie wedge.

Mr. J. S. Dow, in reply, said he had only worked with photometers with wedges of 90°, but he was certain that the cosine law would not hold at acute incidence on account of the large amount of regular reflection.

A paper entitled "*Experiments on the Production of Sand Ripples on the Sea Shore*" was read by Mrs. AYRTON.

The sand-ripples which form so marked a feature of the sea-shore, although parallel to the line of the breakers, are not produced by their edges, but are formed entirely under water. It is difficult to imagine that the long, sweeping, to and fro motion of the sea that one watches from the beach, can produce row after row of quite small ripples, such as are seen in certain places on the beach. Yet it is this long, steady, see-saw motion of the water that produces the ripples, as was first observed in 1882 by Mr. Arthur Hunt.

To show this, a glass trough, six feet long, in which there was level sand, covered with a foot of water, was pushed to and fro on rollers by means of an electromotor. This motion set the water oscillating, and soon small ridges were seen in the sand, at nearly equal distances from one another, growing larger and larger as the oscillation continued.

Twenty years ago, Professor George Darwin discovered that certain vortices that he observed in water oscillating over ripples helped to build the ripples higher, but he left the problem of the *birth* of the ripples practically untouched. He thought that each ripple was started solely by friction, but this suggestion is apparently negatived by the regularity of the ripples, even in their earliest stages. By deduction from the shape of certain sand vortices, it appears that every ridge or furrow in otherwise smooth sand must produce two other ridges, one on either side of

the first, and that these two give rise to two other ripples, one on the right of the right-hand one, and the other on the left of the left-hand one, and so on, till the whole becomes ripple-marked. In other words, it wants but one *single* irregularity, in otherwise smooth sand, to cause the whole sand to become ripple-marked under oscillating water. Experiments were shown to demonstrate this fact.

Next, to show that the vortices generated by the original ripple actually swept out the succeeding ones, an artificial barrier was put across the trough to increase the size of the vortices, a handful of moist black pepper was thrown in, and the water oscillated. Immediately large vortices were seen whirling first on one side of the barrier, and then on the other, hollowing out furrows in the sand, while the great brushes of water that flowed over the vortices swept up new furrows. In fact, the actual process by which the water started and built up the ripples was shown.

Mrs. Ayrton illustrated how the sand ripples on the sea-shore could be exactly imitated, even when the water ran in one direction alone, if only the sand were sloped, as it is on the sea-shore, so that the water ran up it, and if, by means of a paddle, a series of waves were sent along the water in the direction in which it was running—if, in fact, the motion of the incoming tide were imitated. But if the long, surging motion of the sea produces the sand-ripples, why is not the whole of the sandy-shore seen ripple-marked? The answer is that it is all ripple-marked when the tide is high, but the waves at the edge of the retreating tide wipe out the ripples except where there is a pool, so that the water is left over the ripples until after the sea has retired. Further, while the water is oscillating over the sand-ripples, which it has formed, they never remain constant either in height, distance apart, or position. Their heights and distances apart are greater the more violent the oscillation, the longer it has been going on, and the greater the periodic time of the wave and the shallower the water. The greatest depth at which ripple-mark can be formed at the bottom of the sea depends on the violence of the motion of the water. At depths of 60 or 70 feet the sand is said to have been found ripple-marked. If the depth of a vessel is large compared with its cross section, a depth of water can be found beneath which no sand-ripples can be formed. In the case of a pickle-bottle, for example, this limiting depth of water over the sand is an inch or two.

During the whole of the demonstration the water in the 6-foot trough was kept oscillating, and the sand was seen to heap itself up in the form of a large ripple-marked heap at about the middle of the trough, having a contour very unlike that of the sea-shore ripples. On sprinkling a very little sand in the water in a small trough, and rocking it to and fro, the sand was seen to quickly assemble in a straight line across its middle. Watching these grains carefully, it may be noticed that the result arises from every swing carrying each grain on one side of the centre nearer to the middle than the next swing carried it away again. And not only each separate grain of sand, but each ripple as a whole, when ripples have been formed, tends to move towards the middle of the trough. In the 6-foot trough, and in a small trough, the water was kept oscillating so as to form a stationary wave twice the length of the trough, and the place where the heap of sand was formed was where the level of the water changed least and its horizontal velocity was the greatest. In a trough 3 feet long the water was oscillated by means of an electromotor, so that the length of the wave was only two-thirds the length of the trough, so that there were three places where the level changed least, and the horizontal velocity was a maximum, and at each of these three places the sand was seen to heap itself up.

Referring to the Goodwin Sands, which she had had an opportunity of observing, Mrs. Ayrton said she found it impossible to avoid recognising the resemblance between the hillocks and hollows of these sands and those made in her glass troughs, and it seemed, therefore, very possible that they were also produced by stationary waves. If so, then was it not possible, she asked, to imagine some means of altering the trend of the sea so as to keep it from forming the stationary waves which she believed heaped up the Goodwin Sands?

FARADAY SOCIETY.

Ordinary Meeting, June 25th, 1907.

Prof. S. U. Pickering, F.R.S., in the Chair.

General Discussion on Hydrates in Solution.

After some preliminary remarks by the Chairman, the Discussion was opened by Dr. T. Martin Lowry, who read a paper on "*The Thermo-chemistry of Electrolytes in relation to the Hydrate Theory of Ionisation*," by Mr. W. R. Bousfield, M.A., K.C., and himself.

1. The process of ionisation of a neutral salt in aqueous solution "*is usually attended with a development of heat*" (Nernst, "Theoretical Chemistry," 1904, 659), *e.g.*, $KCl \rightarrow \overset{+}{K} + \overset{-}{Cl} + 250$ cals. (Arrhenius, *Zeit. Phys. Chem.*, 1889, iv., 106). It is pointed out that the decomposition of potassium chloride into molecular potassium and molecular chlorine involves an absorption of 105,600 cals., and that a further absorption must accompany the decomposition of the molecules into atoms. The electrification of the atoms is also probably an endothermic action, and the change represented by the above equation, so far from involving the liberation of 250 cals., must actually involve the absorption of more than 100,000 cals.

The process of ionisation must therefore involve some powerful exothermic action not shown in the ordinary scheme, and it is suggested that this is supplied by the combination of the charged atoms or "ionic nuclei" with the solvent to form hydrated ions.

2. A scheme is given whereby the work done in charging the ions, or in separating ions already charged, may be calulated on the assumption that the ions behave as charged conductors immersed in a fluid dielectric. The values deduced for the energy of electrification or of separation range from about 1000 to 8000 cals. per equivalent.

3. It is pointed out that, according to the theory of electrolytic dissociation, the heat of formation of a salt in dilute solution is the sum of the heats of formation of the ions. Values are deduced for the separate ionic heats of formation, and a table is given showing with what remarkable accuracy the additive law holds good; this additive relationship, which does not appear in the heats of formation of the solid salts, affords important evidence in favour of the view that the ions exist independently in dilute solutions.

4. The majority of the heats of formation of the ions are large positive quantities. The energy liberated during the process of ionising an element cannot be due to the disruption of the molecules of the element into atoms, nor to the electrification of these atoms. Both of the above processes appear to be endothermic, and it is again necessary, in order to explain the thermochemical data, to postulate that ionisation is accompanied by some exothermic action not indicated in the symbols—

$$\frac{K_x}{x} \rightarrow \overset{+}{K} \quad \text{or} \quad \frac{Cl_2}{2} \rightarrow \overset{-}{Cl}.$$

This exothermic action is supplied by the combination of the ionic nucleus with the solvent.

Dr. James C. Philip, M.A., Ph.D., D.Sc., read a paper entitled "*Influence of Non-electrolytes and Electrolytes on the Solubility of Gases in Water. The Question of Hydrates in Solution.*"

The author supported the view according to which the diminished power of a solution to dissolve hydrogen and oxygen as compared with pure water is due mainly to the hydration of the solute and the consequent diminution of the "free" solvent. In determining the extent to which

any given solute is hydrated, it is first supposed that the standard absorbing volume is, not 1 litre of the solution, but that volume of the solution which contains 1000 grms. of the pure solvent. In this way values of the average molecular hydration for a number of common salts are obtained. It is found that the average molecular hydration increases with the dilution of the salt solution, and decreases for a given salt solution as the temperature rises.

Dr. GEORGE SENTER read a paper on "*Hydrates in Solution: Discussion of Methods Suggested for Determining Degree of Hydration.*"

It is pointed out that recent attempts to account for the properties of aqueous solution on the basis of association alone have not only proved inadequate to afford a quantitative representation of the facts, but in some respects do not appear to be even in qualitative agreement with experiment.

In forming an opinion as to the relative trustworthiness of different methods which have been suggested for determining the degree of hydration regard must be had to the following considerations: (1) Other things being equal, statical methods are more reliable than dynamical ones; (2) the law of mass action requires that for salts the degree of hydration must increase with dilution up to a point beyond which it remains practically constant on further dilution; (3) if, as is usually the case, hydration is associated with evolution of heat, the complexity of the hydrates must decrease with rise of temperature.

All the different methods indicate that the degree of hydration varies with the atomic weight; for example, in the case of the chlorides of the alkalis, the hydration decreases with increasing atomic weight of the alkali metals. From a quantitative point of view our knowledge of hydration is much less satisfactory, and the results so far obtained must be regarded as of a preliminary character.

A paper communicated by Dr. ALEX. FINDLAY on "*The Stability of Hydrates as Indicated by Equilibrium Curves*" was read in abstract by the Secretary.

From a study of the freezing-point curves of concentrated aqueous solutions conclusions have been drawn, more especially by Biltz and by H. C. Jones, with regard to the existence of hydrates in solution. While the qualitative correctness of the conclusions may be accepted, grave doubts arise as to the correctness of the quantitative formulæ assigned by Jones to the hydrates of different substances. These doubts are due not only to the fact that the conclusions as to hydration were reached (in so far as the freezing-point measurements are concerned) by means of an unjustifiable extension of the van 't Hoff-Raoult law, but also to the fact that certain factors, *e.g.*, heat of dilution, were not taken into account.

While the study of the equilibrium curve of solutions in contact with ice as solid phase (the freezing-point curve) may, on the basis of certain assumptions, give an indication of the "degree of hydration" of the solute, it cannot enable us to decide as to the particular hydrates present, nor the extent to which these hydrates are dissociated chemically.

On the other hand, some insight into the question of the stability of hydrates can be obtained from the study of the equilibrium curves of solutions in contact with the hydrates as solid phase, *i.e.*, what are frequently called solubility curves.

When a compound of two components is capable of existing in contact with solution of the same composition as itself, *i.e.*, when it possesses a definite melting-point, the equilibrium curve of the two-component system will exhibit an intermediate curve, which gives the conditions under which the solid compound can exist in contact with the liquid solution, or homogeneous mixture of the two components. When the compound undergoes chemical dissociation at the temperature of the melting-point, it is found that the equilibrium curve has a rounded summit, and the greater the degree of dissociation the flatter is the summit of the curve. Conversely, the sharper the summit of the curve the less the degree of dissociation. From the appearance of the curve alone, then, some idea of the stability of the compound can be obtained.

If, now, we regard the presence of the products of dissociation as causing a lowering of the freezing-point of the pure compound, and if we regard the lowering produced to be in accordance with the van 't Hoff-Raoult law, then, from a knowledge of the molecular depression of the compound, it is possible to calculate the course of the freezing-point curve of the compound for different degrees of dissociation. The experimentally determined equilibrium curve is compared with the curve so obtained, and thus an approximate knowledge obtained of the degree of dissociation of the compound.

It must be pointed out that this method of determining the degree of dissociation is only an approximate one, for it depends on various assumptions which cannot be regarded as being more than approximately fulfilled. The chief of these assumptions are:—(1) the validity of the van 't Hoff-Raoult law, (2) the validity of the law of mass action in concentrated solution, (3) the degree of dissociation is independent of the temperature.

So far calculations have been carried out only in the case of organic binary compounds; but the method can also be applied to the case of salt hydrates, although in this case the above assumptions are less likely to be fulfilled.

Prof. W. A. TILDEN, F.R.S., referred to the fact that in crystals it appeared to be the metal only which detained the water of crystallisation. In many cases, such as that of ammonia dissolved in water, where ammonia as such was also present, the hydrate theory could not be adopted as it stood. There was, in fact, no single theory at present able to explain all the phenomena observed.

Mr. CALDWELL criticised the various methods used for measuring hydration. In the experiments of Jones, for example, whose method was open to objection, many of the results did not follow what would be expected from the law of mass action. Philip assumed that the dissolution of a gas was mechanical and that of a salt chemical. If that were true a gas of small molecular weight, such as helium, should be readily soluble.

Mr. W. A. DAVIS said that there were many cases of solution, *e.g.*, in dyeing, which were covered by neither the ionic nor the hydration theory, but in which the process was purely mechanical.

Mr. FENTON said that it was not always very clear what was meant by a hydrate. The methods hitherto employed for studying hydrates were chiefly physical, and the results obtained were capable of many interpretations. The problem should be studied in such a way that specific chemical properties were obtained.

In reply to Dr. H. Borns, Dr. LOWRY said he imagined ionisation to be the result of the separate hydration of the ionic constituents of the molecule.

The CHAIRMAN thought that the agreement between the heat of formation of a salt in dilute solution and the sum of the separate heats of formation of the ions shown to exist by Mr. Bousfield and Dr. Lowry proved nothing, as the proof involved reasoning in a circle. In reply, the authors explained that the agreement proved these properties of the ions to be additive, and so gave further support to the dissociation hypothesis.

Battersea Polytechnic.—The Governing Body of the Battersea Polytechnic have appointed Mr. S. G. Rawson, D.Sc. (Lond.), F.I.C., Principal of the Polytechnic in succession to Mr. Sidney H. Wells, who has been Principal since the foundation of the institute in 1893, and is resigning to take up the position of Director-General of the Department of Agriculture and Technical Education for Egypt. Dr. Rawson is at present Director of Education for Worcestershire, and was formerly Principal of the Technical College, Huddersfield, and Lecturer at Liverpool University.

OBITUARY.

SIR WILLIAM HENRY PERKIN, F.R.S.

THE news of the death of Sir William Perkin, of pneumonia and appendicitis, after an illness of four days' duration, will be received with the deepest regret by the whole scientific world. His researches have made his name universally known and revered, while in those who enjoyed the advantage of personal acquaintance with him his singularly charming disposition evoked no less admiration.

Sir William Perkin, who received the honour of knighthood last year, was the youngest son of Mr. G. F. Perkin, and was born in London in 1838. He was educated at the City of London School, and passed thence to the Royal College of Chemistry, where his conspicuous ability soon brought him prominently before the Principal, Professor Hofmann, who soon after his entrance appointed him to the post of private assistant, and in every respect did his utmost to stimulate and direct the ambitions of the boy. Perkin had from the beginning been deeply interested in chemistry, and the influence of Professor Hofmann was soon sufficient to increase his liking to a passion, in the pursuit of which his ardour knew no flagging, and from the very early days of his career as a student of the College he devoted much of his spare time and energy to the study of various problems which the course of lectures he was attending suggested to his active mind. During one vacation he was studying the synthesis of quinine, when he found that the oxidation of aniline with potassium bichromate and sulphuric acid led to the formation of a dye, mauvëine, afterwards shown to be phenyl-safranine. When a favourable opinion of the value of this new colouring matter had been expressed by dye experts, in spite of the many difficulties with which he was confronted, Perkin, with the aid of his father and brothers, established a factory at Greenford Green, near Harrow, in which the new substance could be prepared on a large scale, and within a year of its discovery he succeeded in placing it upon the market—a remarkable achievement indeed for a youth of eighteen. The discovery of mauve gave a great impetus to the investigation of coal-tar and its derivatives, and laid the foundation of the most important of scientific industries. Perkin's work was soon followed by researches, undertaken by the chemists of all nations, and leading to the discovery of various derivatives of triphenyl-methane.

Meanwhile he was pursuing the investigation of different classes of organic substances, and was showing particular skill in devising and perfecting new methods of synthesis. Thus he found that by the action of aromatic aldehydes upon the salts of fatty acids it was possible to synthesise unsaturated acids, and this reaction, which is now known by his name, has led to important developments in technical chemistry. When he applied it to salicylic acid and sodium acetate he obtained the sodium salt of coumaric acid, and from the latter by elimination of water the anhydride coumarin is prepared. This substance was the first natural perfume prepared synthetically, and Perkin was thus instrumental in setting on foot the artificial perfume industry. The study of these condensation reactions is still yielding rich fruit, both from a purely scientific and a commercial point of view. Another dye manufactured for the first time on a commercially remunerative scale in the Greenford factory was madder red or alizarin, the laboratory preparation of which from anthracene had been discovered by Graebe and Liebermann, and turned to practical account by Perkin. Moreover, his work upon the rotation of the plane of polarisation by a magnet, and upon the relations between magnetic polarisation and chemical constitution, has brought to light some important facts.

Enough has been said of some of the more striking results of Perkin's work to indicate how he possessed a remarkable power of recognising the commercial possibilities of scientific work, while at the same time he never ceased in his allegiance to purely scientific research, and of late years had devoted himself exclusively to it. He discovered and threw valuable light upon the constitution of many substances of great importance in organic chemistry, and thus did much to further its development from a purely theoretical point of view. It is, perhaps, unnecessary to recall how honours of all descriptions were showered upon him, reaching their culminating point last July in the Jubilee celebration of the foundation of the coal-tar industry, when he received gratifying evidences of the esteem and admiration felt for him by the whole scientific world. A presentation of his portrait, which now becomes the property of the nation, of addresses from many scientific institutions of all nations, and the foundation of a fund for the promotion of chemical research, to be known by his name, were among the practical manifestations of the regard in which he was held, while various marks of recognition of his valuable work were received by him from foreign chemical societies, and the universities of all nations vied with one another in conferring honorary degrees upon him.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxliv., No. 24, June 17, 1907.

Preparation of Anhydrous Lithium Oxide.—M. de Forcrand.—If the heat of solution of lithium oxide is taken as 26 cals. (Béketoff) and 8·96 cals. for the solution of $Li_2O.H_2O$ or 2LiOH, by difference $Li_2O(sol.) + H_2O(liq.) = 2LiOH(sol.) + 17·04$ cals. From this it would appear that the dehydration of lithium hydroxide by heat would give the anydrous oxide, Li_2O. Thus, adding 9·66 cals., the heat of formation of H_2O gas, we get 26·70 cals. for the reaction $Li_2O + H_2O(gas) = Li_2O.H_2O(sol.)$. Now, $\frac{26,700}{30} =$ 890° (abs.) = 617° C. Thus, LiOH should boil at 617°, and if the water vapour generated were removed by an inert gas the complete dehydration should be effected below 600°. These theoretical considerations have been confirmed by the experimental facts. If pure commercial lithium hydroxide or the crystalline secondary hydrate, $LiOH.H_2O$, is heated in a current of hydrogen at a temperature of 660°, the dehydration commences rapidly, then slackens, and is complete after seven or eight hours. At 780° the same result is obtained in one hour. There is no loss by volatilisation, and the platinum boat in which the operation is carried out is unaffected, though at 800° or 820° a loss of weight can be detected. The substance thus obtained is absolutely white, not crystalline but porous; its analysis gives the formula Li_2O exactly.

Absolute Atomic Weight of Manganese.—Gustavus D. Hinrichs.—Baxter and Hines find for the atomic weight of manganese 54·951 to 54·959, *i.e.*, approximately 0·05 below 55. If Ag = 108, Br = 80, Mn = 55, the value $\frac{2Ag}{MnBr_2} = 1·00465$ change = −47, variation = 2·13. It is then found that Baxter and Hines' experiments give a mean variation of −1 in the fifth decimal place of the ratio $Ag : MnBr_2$. Thus, the absolute atomic weight of manganese is 55 according to Baxter and Hines' fifteen experiments, when they are examined by the author's method. It is interesting to notice that the very small variations differ in magnitude and even in sign according to the degree of purity and origin of the material used, which goes to prove the accidental nature of these deviations. The second series of experiments in which the ratio

$\frac{2AgBr}{AgBr_2}$ was determined gave a change of −82 and a variation of +1·22 (for 0·1 in manganese), and thus the agreement was not so good as in the first series, probably because the reaction is too complex.

Arsenic and Methyl Arsenic Acids.—E. Baud and A. Astruc.—The authors have determined the heats of solution of pure arsenic acid and its anhydrous sodium salts, as well as the heat of neutralisation of the dissolved acid by one, two, or three molecules of soda in solution. For arsenic acid the numbers obtained are:—

$AsO_4H_3(sol.) + Na(sol.) = H(gas) + AsO_4NaH_2(sol.)$ +57·15 cals.

$ASO_4NaH_2(sol.) + Na(sol.) = H(gas) + AsO_4Na_2H(sol.)$ +45·87 cals.

$AsO_4Na_2H(sol.) + Na(sol.) = H(gas) + AsO_4Na_3(sol.)$ +40·76 cals.

Arsenic acid is therefore a little less acid than phosphoric acid, but the difference is relatively small. For cacodylic acid

$$O=As\begin{matrix}CH_3\\CH_3(sol.)\\CH_3\end{matrix} + Na(sol.) = H(gas) + OAs\begin{matrix}CH_3\\CH_3(sol.)\\ONa\end{matrix}$$ +41·72 cals.

Thus, the following results have been obtained:—(1) Mean acidity of arsenic acid, 47·92 cals.; (2) mean acidity of monomethyl arsenic acid, 44·705 cals.; (3) mean acidity of cacodylic acid, 41·72 cals. Hence, the fixation of a CH_3-group to the atom of arsenic diminishes the acidity of arsenic acid by 3·22 cals., and the fixation of a second group again lowers it by 2·98 cals. These numbers agree perfectly with the rule suggested by De Forcrand for the acidity of alcohols.

Action of Fluorine on Selenium in presence of Glass.—Paul Lebeau.—The author's chief reason for believing that Prideaux's hexafluoride of selenium is really an oxyfluoride is the fact that when the gas from several preparations is fractionated in such a way as to collect in different flasks the more or less volatile products, a decided difference of density is found in the contents of the flasks—the first portions have a density of about 6·59 (the theoretical density), while in the last portions it falls as low as 6·28. From a chemical point of view the analysis of the gas presents special difficulties, but the author hopes to communicate shortly the results of his experiments.

Solubility of Alumina in Aluminium Sulphide and of Magnesia in Magnesium Sulphide.—Marcel Houdard.—If aluminium sulphide is fused with alumina in an electric furnace and the melt is treated with dilute hydrochloric acid, an insoluble crystalline residue of alumina remains behind. If the mass is allowed to cool sufficiently slowly, rhombohedric crystals are obtained. Attempts to colour these crystals have not as yet been successful. Crystals of magnesia can be prepared similarly. Concentrated hydrochloric and nitric acids slowly dissolve crystalline magnesia when warmed; sulphuric acid acts upon it in the cold. The crystals are cubic, and have no action on polarised light.

Glycol of Anethol. Transformation into Anisylacetone.—MM. Tiffeneau and Daufresne.—If an acetic solution of anethol dibromide is boiled with zinc acetate a molecular transposition occurs, and *p*-methoxyhydratropic aldehyde is formed:—

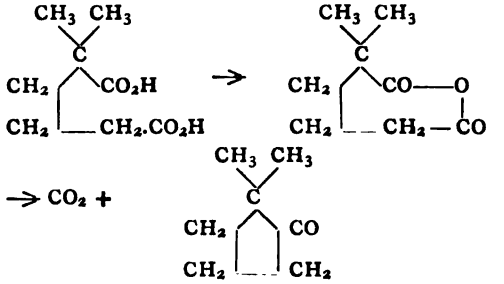
$$OCH_3—C_6H_4—CH_2(CO_2—CH_3)—CHBr—CH_3 \xrightarrow{-HBr} OCH_3—C_6H_4—CH_2(CO_2—CH_3)—C{=}CH_2$$

$$\rightarrow OCH_3—C_6H_4—C(CH_3){=}CH—CO_2—CH_3) \xrightarrow{+CH_3CO_2H} OCH_3—C_6H_4—CH\begin{matrix}CH(CO_2CH_3)_2\\CH_3\end{matrix}.$$

The saponification of this diacetic ether gives directly the glycol of anethol, fusing at 116°. When distilled *in vacuo* it loses water, yielding a crystalline compound which seems to be the corresponding diethylene oxide. The authors submitted this glycol to the action of sulphuric acid and investigated the product obtained. Silver oxide transforms it into anisic acid; with iodine and caustic potash it gives iodoform and methoxyphenylacetic acid. Its semicarbazone and oxime fuse at 175° and 74° respectively. Hence, the glycol of anethol is transformed into anisylacetone according to the equation:—

$$OCH_3—C_6H_4—CHOH—CHOH—CH_3 = H_2O + OCH_3—C_6H_4—CH_2—CO—CH_3.$$

New Method of Converting Substituted Adipic and Pimelic Acids into Cyclic Compounds.—H. G. Blanc.—The method of passing from dibasic acids to the corresponding cyclic ketones by calcination of the calcium salts is inconvenient from many points of view. The author finds that it is both simpler and quicker to heat the acid (*e.g.*, substituted adipic acid) for some hours with acetic anhydride, thus getting the anhydride. Then the excess of acetic anhydride is driven off *in vacuo*, and the anhydride of the dibasic acid is decomposed by slow distillation at ordinary pressure:—



The yield with adipic and pimelic acids is not very satisfactory (about 50 per cent of the theory), possibly because the ketones readily condense. The author has thus prepared some new ketones, which form the starting-point for the synthesis of terpene derivatives.

Dimagnesium Compound of Dibromopentane-1.5.—V. Grignard and G. Vignon.—Dibromopentane in presence of anhydrous ether reacts easily with powdered magnesium, giving a magnesium compound, hardly soluble in ether, which separates as a slightly coloured mobile liquid. Carbon dioxide is absorbed in the cold with a slight evolution of heat, and a crystalline mass forms in the lower liquid layer. From this an acid and a neutral portion can be separated. The latter distils at 50—52° under 12 mm. pressure, and cyclohexanone is the principal product of the reaction. When the acid portion precipitated from its sodium salt is fractionated, from the product may be separated dimethylene dicarboxylic acid. The equations are:—

$$CH_2\begin{matrix}CH_2—CH_2MgBr\\CH_2—CH_2MgBr\end{matrix} + CO_2 = CH_2\begin{matrix}CH_2—CH_2\\CH_2—CH_2\end{matrix}C\begin{matrix}OMgBr\\OMgBr\end{matrix}$$

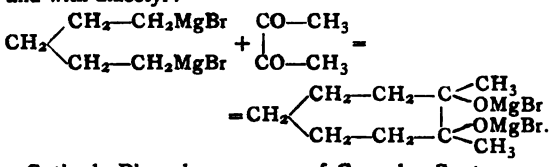
$$\rightarrow C_6H_{10}O + MgBr_2 + MgO$$

$$CH_2\begin{matrix}CH_2—CH_2MgBr\\CH_2—CH_2MgBr\end{matrix} + 2CO_2 = CH_2\begin{matrix}CH_2—CH_2—CO_2MgBr\\CH_2—CH_2—CO_2MgBr\end{matrix}.$$

With ethyl acetate the dimagnesium compound undergoes the following reaction:—

$$CH_2\begin{matrix}CH_2—CH_2MgBr\\CH_2—CH_2MgBr\end{matrix} + CH_3CO_2C_2H_5 = CH_2\begin{matrix}CH_2—CH_2\\CH_2—CH_2\end{matrix}C\begin{matrix}OMgBr\\CH_3\end{matrix} + C_2H_5OMgBr.$$

and with diacetyl :—



Cathode Phosphorescence of Complex Systems.—G. Urbain and Clair Seal.—The authors have studied the phenomena of cathodic phosphorescence in mixtures with the following results :—*Coloured Mixtures.*—The presence of coloured oxides (of terbium or praseodymium) diminishes the phosphorescence due to other substances, the influence of terbium oxide being much greater than that of praseodymium. Samarium oxide and dysprosium oxide, which are nearly white, mask the phosphorescence of the black oxide of praseodymium, but to a lower degree than black terbium oxide. The maximum of phosphorescence due to each substance in a ternary system corresponds to the percentage of substance necessary to produce the maximum in binary systems with the same diluent. The maximum is less bright in a ternary than in a binary system. Spectral variations due to dilution are the same in binary as in ternary systems. *Colourless Mixtures.*—The oxides of praseodymium and terbium, which are black, are necessarily very absorbent, but their salts behave practically like colourless substances in ternary phosphorescent mixtures. The phenomena due to dilution and to the reciprocal independence of the maxima are the same in these mixtures, but the salts of praseodymium do not mask the phosphorescence of samarium, terbium, and dysprosium. On the contrary, the salts of these last three elements mask not only praseodymium but also the other rare earths.

MISCELLANEOUS.

Queen's College, Galway.—Mr. Percy Corlett Austin, M.A., of Queen's College, Galway, has just been awarded a Science Research Scholarship in Organic Chemistry by His Majesty's Commissioners for the Exhibition of 1851; and Mr. William Goodwin, B.Sc., Ph.D., a former 1851 Exhibition Research Scholar of Queen's College, Galway, has been appointed Lecturer in Chemistry at the South-Eastern Agricultural College, Wye, Kent.

Society of Arts.—The Council of the Society of Arts have awarded medals to the following readers of Papers at the meetings of the Session just concluded :—

To Mr. John William Gordon, for his paper on "Patent Law Reform."

To Colonel Sir Charles M. Watson, K.C.M.G., CB., for his paper on "Some Objections to the Compulsory Introduction of the Metric System."

To Mr. Albert E. Humphries, for his paper on "Modern Developments of Flour-milling."

To M. Philippe Bunau-Varilla, for his paper on "The Panama Canal—the 'Lock Canal' type and the 'Straits of Panama' type."

To Mr. Arthur E. Morton, for his paper on "Modern Type-writers and Accessories."

To Mr. Noel Heaton, B.Sc., for his paper on "Mediæval Stained Glass, its Production and Decay."

To Mr. Herbert Wright, for his paper on "Rubber Cultivation in the British Empire."

Mr. Alfred Edward Carey, M.Inst.C.E., for his paper on "The Protection of Sea Shores from Erosion."

To Mr. A. Yusuf-Ali, M.A., LL.M., I.C.S., for his paper on "The Indian Mohammedans — their Past, Present, and Future."

To Captain E. Barnes, for his paper on "The Bhils of Western India."

To Sir Frederic S. P. Lely, K.C.I.E., C.S.I., for his paper on "The Practical Side of Famine in India."

To Mr. Laurence Robertson, I.C.S., for his paper on "Irrigation Colonies in India."

To Mr. George Wilson, C.B., for his paper on "The Progress of the Uganda Protectorate."

To Hon. John Winthrop Hackett, LL.D., for his paper on "Social and Economic Conditions in Australia."

To Mr. Thomas Okey, for his paper on "Basket Making."

To Mr. William Dale, F.S.A., for his paper on "Artistic Treatment of the Exterior of the Pianoforte."

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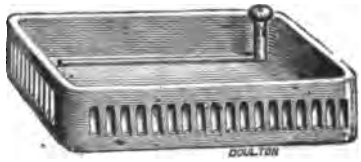

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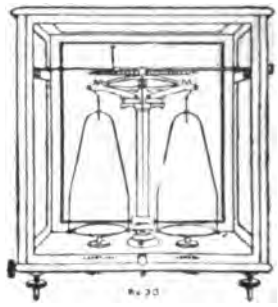

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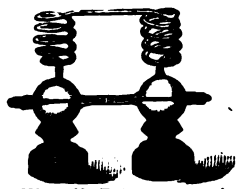

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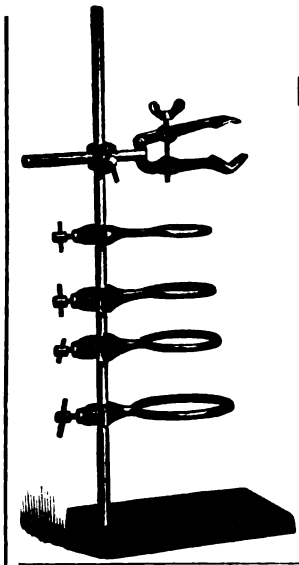

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VULCANISATION TESTS WITH PLANTATION RUBBERS.

By CLAYTON BEADLE and HENRY P. STEVENS.

WHEN a raw material which for many years has formed the staple of a large industry is by force of circumstances produced in new districts and by new methods, the manufacturer naturally asks himself whether his new sources of supply are suitable to his methods of manufacture. He may, of course, have no difficulty in determining which of the products (*i.e.*, from old or new sources) is best suited to his *existing* methods, which methods are the result of a long experience with his original sources of supply; but it becomes ultimately a question as to which product will suit him best in the long run if both are worked under the most favourable conditions.

This is the state of affairs in which the rubber industry in the course of time will find itself, or more particularly that branch of the industry which deals with the production of high-class rubber articles of which para-rubber is an important ingredient. Up to within the last three or four years the world drew its supply of raw rubber from trees growing wild in various tropical areas. Some ten years ago a beginning was made with planting—particularly in the Malay Peninsula, and later in Ceylon—chiefly with *Hevea Braziliensis*, or the para-rubber tree, but as no commercial yield of rubber is obtained until the tree reaches its fifth or sixth year the effect of this planting is only just beginning to be felt, and the imported plantation rubber at the present time only forms about 1 per cent of the total production. From the large areas now in process of being opened up, this production must increase considerably in the course of the next ten or fifteen years, until eventually the plantation rubber forms a considerable proportion of the supplies to rubber manufacturers.

The properties of rubber are not only dependent upon such things as soil, locality, climate, &c., but are largely affected by the methods used in curing and preparing it for the market, and as the methods of coagulation and preparation differ radically from those used in the case of wild rubbers this consideration particularly applies to plantation rubber. Without going into any details it may be stated that in the former case the methods are primitive and inadequate, except in the case of the smoked rubbers, while the planters by commonsense precautions, and in some cases by the use of simple coagulating, washing, and drying plant, have sent to this country consignments which are unequalled from the point of view of purity and general excellence. It has, however, been asserted, without apparent reason, that, in spite of these desirable qualities, the plantation rubber is wanting in the "nerve" especially attributed to hard cure para.

The object of the present paper is the discussion of a number of preliminary tests made with the plantation rubber with a view to testing its qualities and comparing it with a typical high-class rubber, such as hard cure Amazonian para. The methods employed in valuation of rubbers as carried out by brokers and merchants would be useless for this purpose. The broker looks for adulterants, and tests the physical qualities by the general appearance, smell, and feel of the rubber. Such tests cannot, except in the roughest manner, be of any value in forming an estimate of the qualities of plantation or any other rubber from a manufacturer's standpoint. A carefully conducted chemical analysis will, however, be of some help.

It is obvious, to begin with, that the value of a crude rubber to the manufacturer will to a large extent depend upon the proportion of actual rubber substance or caoutchouc it contains (see Heil and Esch, "Handbuch der Gumm Warenfabrikation," p. 40). A crude rubber, such as hard-cure para, will contain certain substances normally present in the latex from which it was obtained; of these the most important are resin and protein or nitrogenous bodies. It may also contain extraneous substances, such as sand and dirt of all kinds, and finally it will always contain more or less water. It is usual to determine these constituents and by difference to calculate the amount of caoutchouc, there being no agreed satisfactory method of directly estimating the latter. It has been suggested that a further examination should be made of the resin and protein bodies with a view to characterising them more exactly; but, quite apart from the large amount of research work which will be necessary before this can be done, it is difficult to see what advantage will be gained except for the purpose of distinguishing the source of the rubber; in any case it is doubtful if the results would justify the additional work entailed in the analysis.

Table I. gives the analysis of a typical hard-cure para and that of a plantation "block"; the latter represents the mean of numerous analyses we have made from time to time on good qualities of this product.

TABLE I.

	Hard-cure para.	Plantation "block," as imported.
Moisture	12·7	0·4
Resins..	3·1	4·0
Protein	2·9	2·8
Ash	0·3	0·1
Caoutchouc (by difference)	81·0	92·7

It will be seen that the figures are distinctly in favour of the plantation product; the moisture is particularly low in the latter owing to its having undergone a systematic drying process. This has the great advantage that the rubber is much less likely to undergo putrefactive change during transport through hot climates—as everyone knows—moulds and bacteria must have moisture for their growth and development. The samples we have examined of properly prepared wild rubber all contained large quantities of water, such as from 10 or 12 per cent. Of course, plantation rubber which is merely air-dried, as in the form of biscuits, may contain more than one-half per cent moisture, but the amount will not be excessive.

So far, then, as the analyses go, the figures are in favour of the plantation, and this has found due recognition on the market, where the best dry block, crepe, and other forms have fetched a higher price than hard cure para, practically in proportion to the percentage of real rubber that these products contain. It may, however, be questioned whether a greater difference in price is not justifiable and will be obtained in favour of plantation rubber when the advantages of a pure and regular product are better recognised and manufacturers have acquired greater experience and confidence in handling it.

As the best block, crepe, and sheet are washed in a two-roll washing machine immediately after coagulating, and then dried either in the air or in vacuum drying ovens, and this treatment on the spot is becoming very general, it seems reasonable to suppose that the manufacturer in this country should be able to take this washed and dried product and use it straight away in his mixing machines without any preliminary treatment. On the other hand, all ordinary grades of wild rubber when received by the manufacturer are too impure and contain too much moisture for use right away; they have therefore first to be subjected to a washing process in which the rubber is torn to shreds, in the course of which its "nerve" is affected, and then subsequently to be submitted to a tedious drying process, and if possible storage, in order that the rubber may regain

some of the physical properties it has lost on treatment. Not only is it natural to suppose that all this can be avoided by the use of rubber washed and dried on the plantation, but the loss incurred in the washing process is also avoided. This loss in the case of the best wild rubbers, such as hard-cure para, amounts to from 13 to 17 per cent.

In order to test the value of plantation grown and plantation prepared rubbers, something more is required than chemical analysis. As for practical purposes it may be said that all rubber is vulcanised in the course of manufacture, and as the properties of vulcanised rubber are very different from the raw article, it appeared to us that the only satisfactory means of determining the value of plantation rubber was to vulcanise it, and carry out physical and chemical tests on the vulcanised product. Moreover, in order to eliminate as far as possible the effect of carrying out such vulcanisation on a laboratory instead of on a manufacturing scale, we made a number of parallel experiments with a sample of typical hard-cure para, which was treated throughout in an exactly similar manner to the plantation rubber. Not only can we test the qualities of plantation rubber in this manner, but we are able to put to the test the possibility of mixing and vulcanising washed and dried plantation rubber without any preliminary treatment.

The hard-cure para was, of course, washed and dried previous to vulcanising, as no results could be got with a product containing moisture. To accomplish this, the wild rubber was cut up, soaked in luke-warm water for some time, and then disintegrated and torn up to shreds in a stream of water, after which it was dried first in air, and subsequently in a desiccator, where it was preserved during the course of the experiments. By these means we imitated as far as possible the methods of purification employed by manufacturers.

The masticating and mixing operations were carried out in a specially equipped machine, which was found well suited for treating small quantities for experimental purposes, and no difficulty was experienced in obtaining a thoroughly even and homogeneous mass. The machine was arranged so that it could be steam heated and kept under proper control. As some of the experimental results obtained by Continental workers are open to criticism owing to the small amount of material used, in our experiments not less than 50 grms. of material were operated upon at a time to minimise any error due to loss of sulphur or loading to be incorporated with the rubber. Some Continental authorities have taken 5 grms. of rubber per mixing. Under such circumstances a loss of finely powdered sulphur or mineral is sure to take place; when the quantities operated on are very small the percentage loss may be considerable. Thus, 5 grms. of rubber would require, say, only 0·3 grm. of sulphur, and a loss of 0·05 grm. would reduce the percentage of sulphur incorporated with the rubber from 6 to 5 per cent; such a difference would entirely vitiate the results. As the amount of mastication very considerably influences the nature of the product in comparative tests, the mastication and mixing was continued for the same length of time. It has been shown that prolonged mastication will increase the acetone soluble products (so-called resins) by as much as 1 per cent. This matter, however, requires further investigation. In most cases when working with plantation rubbers without the addition of mineral matter, the treatment during mastication and mixing seems to have more effect on the product than the time of vulcanisation, provided that it is kept within the usual safe limits; that is to say, it would appear that changing from two to three and four hours' vulcanisation had a smaller influence on the tensile strength of the product than a difference in treatment in mastication and mixing. These points require more experimental work, which is in progress, but will not be discussed in this paper. We shall merely deal here with the general results.

The mixture, after kneading and while still hot, was forced into an iron cylinder. The bottom of the cylinder was closed with a screw-cap, and by means of a steel plunger the mixing was compressed into a solid cylindrical block of such a size that slices could be cut off to fit into the vulcanising moulds. The moulds are of similar construction to those used on a large scale.

On a manufacturing scale it is usual to give the digester a gradual "rise"; that is to say, the temperature is never suddenly raised, but is taken up to one corresponding to a certain pressure, say, for one hour before raising it further. We have tried both slow and rapid methods with mixings containing little or no mineral, and have not found the gradual raising of the temperature to influence the strength of the product to any very marked degree. On the other hand, care, of course, must be taken to keep the temperature within certain defined limits.

For tensile strengths much difficulty was experienced in testing small strips, owing to the tendency of the rubber to tear and rupture in the jaw, even when the ends were cut considerably wider than the middle portion. Eventually the difficulty was got over by punching small rings, which were stretched between smooth round iron hooks. The testing machine was constructed on the well-known principle used in testing cement and other materials, where a regular stream of water or shot is allowed to run into a vessel and the supply cut off automatically the moment of rupture. All figures given are the mean of at least ten tests.

Having briefly described the experimental methods employed we now proceed to give a short *résumé* of the results so far obtained.

The products prepared from plantation rubber were of a beautifully clear transparent yellow to brown shade when viewed through sheets 1 mm. thick. Those prepared from hard-cure para were much darker and less transparent. When vulcanised for a short time the surface sulphured up in the ordinary manner. In the course of our work so far we have carried out over 150 vulcanisations. We have subjected twenty separately vulcanised samples of plantation rubber containing only rubber and sulphur without mineral or other additions to tests for tensile strength and elongation at the moment of rupture, details of which are given in Table II.

TABLE II.—*Tests on Vulcanised Plantation Rubbers.*

Vulcanisation reference number.		Sulphur, per cent.	Tensile strength, in grms.		Elongation at rupture when original = 1·0.		Elongation under a strain 1500 grms. when original = 1·0.	
48			3129		—		—	
49	L	6	3574	3278	13·4	13·0	8·7	8·3
62			3133		12·7		8·0	
74			2882		13·9		—	
77	Q	6	3015	2933	13·3	13·4	9·4	9·7
79			2910		13·2		9·4	
80			2927		13·1		10·2	
83			3164		12·4		8·2	
85	R	6	3263	3264	12·4	12·5	8·0	8·9
87			3366		12·7		9·5	
99			3320		13·3		8·5	
104	T	6	3168	3349	12·5	12·9	8·2	8·2
92			3499		13·1		7·9	
94			3410		12·9		8·2	
143	D2	6	3260	3120	13·4	13·4	10·2	10·4
144			2981		13·4		10·6	
101			3138		13·7		10·4	
45	K	5	3428	3245	14·3	14·0	9·5	10·1
139			3169		13·9		10·4	
110	X	8	3324	3324	12·0	12·0	7·7	7·7
Mean of all tests			3203		13·1		9·0	
Mean of L, Q, R, T, and D2			3187		13·0		8·9	

Taking first the tensile strength in grms. required to rupture the rings, the average of the whole series works out to 3203, and the elongation at the moment of rupture 13·1 per cent. Of these samples, sixteen were vulcanised with 6 per cent of sulphur, and gave an average strength of 3187 grms. and an elongation of 13·0 per cent. Three vulcanised products (K) containing 5 per cent of sulphur were tested, and gave an average tensile strength of 3245 grms. and elongation 14 per cent, while the sample vulcanised with 8 per cent gave a tensile strength of 3324 grms. and elongation of 12 per cent. Although the figures for tensile strength of K and X are somewhat higher than the average of the remainder (3187), we do not attach great importance to this, as this latter average is pulled down by the uniformly low results obtained with mixing Q, and due to some irregularity in the mixing process. On the other hand, it is noteworthy that K (with 5 per cent sulphur) gives a greater elongation (14·0 per cent) than the average (13·0 per cent), while X (with 0·8 per cent of sulphur) gives a smaller elongation (12·0 per cent).

We come now to vulcanising tests with fine hard cure para. We are indebted to Mr. Devitt, jun., of the firm of Lewis and Peat, for supplying us with a quantity of a good average sample of the above, and valued early in March last at 5s. 1d. per pound. (The analysis of this sample is given above). After washing and drying, the mixing and vulcanisation of the samples was carried out in exactly the same manner as with the plantation rubber. The results of the tests are given in Table III.

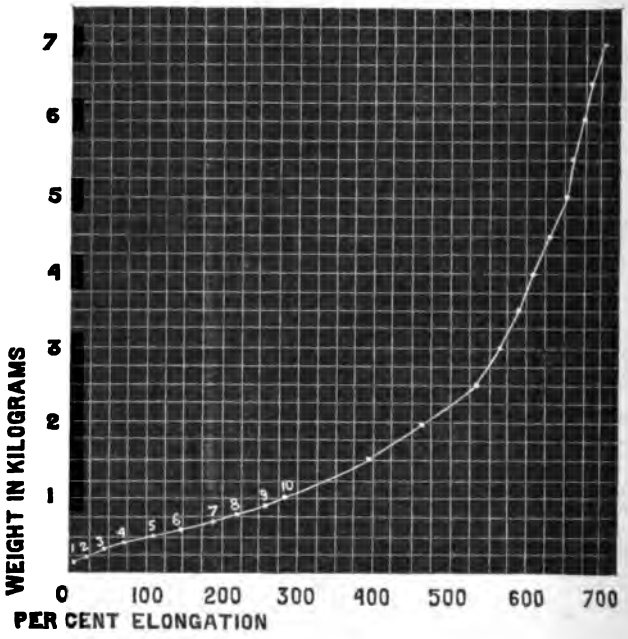
TABLE III.—*Tests on Vulcanised Hard-cure Para.*

Vulcanisation reference number.		Sulphur, per cent.	Tensile strength, in grms.		Elongation at rupture when original = 1·0.		Elongation under a strain of 1500 grms. when original = 1·0.	
95			2788		12·2		9·2	
97	U	6	3541	3164	12·8	12·5	8·3	8·7
114			2646		13·3		10·1	
115	Y	6	2970	2808	12·4	12·8	9·8	9·9
124	S	6	3118	3118	12·9	12·9	9·3	9·3
Mean of all tests			3013		12·7		9·3	

It will be seen that the average tensile strength of five vulcanisations, comprising three mixings, in all of which 6 per cent sulphur was used, averages 3013 grms. and the elongation 12·7 per cent. Both figures are somewhat lower than those obtained with the plantation rubber. The figures, too, are more irregular. It is far from our intention to draw rigorous conclusions from these series of tests, and we do not infer that caoutchouc in the plantation para is superior to that in the Amazonian hard cure para merely because in an average of a number of tests we have obtained slightly better figures with the former. It should be remembered that a certain treatment in mixing and vulcanising which would bring out the best qualities of plantation rubber might require some modification when applied to the hard cure product. On the other hand, we have avoided such objections as far as possible by varying the conditions, such as the duration and temperature, of vulcanisation so as to bring out the best results in both cases.

A considerable amount of work on these lines is in progress, and we hope before long to be in position to publish the results of further tests; we think, however, that with the results so far obtained we are justified in concluding that the rubber of the plantation products will prove to be at least as good if not superior to that of the Amazonian product. So far, we find that the statements frequently made in some quarters that plantation rubber is wanting in "nerve" is not justified by tests we have made on the vulcanised product obtained from the best prepared block.

We have examined the distensibility of vulcanised plantation rubber under increasing strain, and the results are plotted in the form of a curve (see Fig.).



As in the tensile strength tests, a sheet of rubber 1 mm. thick was cut in the form of a ring 40 mm. in diameter and 2·5 mm. wide. It was stretched vertically between smooth iron hooks, the upper one being fixed and the lower one carrying a scale pan. Two marks were made on the band, and the distance between them measured as weights were put into the pan.

We have also made some preliminary tests on sheets of block rubber containing mineral matter, two of which we give below. Mixing M consisted of 50 grms. caoutchouc, 4 grms. sulphur, 10 grms. zinc oxide, 25 grms. lithopone, and 1 grm. pitch; that is, approximately,—

Caoutchouc	56 per cent
Zinc oxide	11 ,,
Lithopone	28 ,,
Pitch	1 ,,

and sulphur, 8 per cent, reckoned on the caoutchouc.

Mixing J consisted of 50 grms. of plantation block caoutchouc, 5 grms. sulphide of antimony, and 2 grms. sulphur. The results obtained are given in Table IV.

TABLE IV.—*Tests on Plantation Rubbers, prepared from "Block," containing Mineral Matter.*

Vulcanisation reference number.	Mixing.	Tensile strength, in grms.	Elongation at rupture, per cent	Elongation under a strain of 1500 grms.
58	M	4746	9·9	6·0
54	J	3915	11·7	6·1

The addition of mineral matter has had the effect of increasing the tensile strength while reducing the elongation. This effect is quite general within certain limits, and further tests are being carried out in which we are investigating the influence of definite quantities of mineral matters on mixings containing plantation block on the one hand and hard-cure para on the other.

ON THE COLOUR REACTIONS OF THE LIGNO-CELLULOSES.*

By C. F. CROSS, E. J. BEVAN, and J. F. BRIGGS.

OF the many characteristic colour reactions of the ligno-celluloses, two have attracted particular attention as the basis of methods of quantitative estimations of mechanical wood-pulp as a constituent of papers. These two reactions—(*a*) with phloroglucol in presence of HCl, and (*b*) with dimethyl *p*-phenylene diamine—are in obvious contrast, and are typical of groups of reactions with phenols and with aromatic bases respectively.

We have found these reactions of service in localising reactive groups of the ligno-celluloses, and generally in pursuing our investigations of these complex plant products.

As a preliminary, we have found it necessary to further investigate the reactions themselves, to determine—(*a*) whether they are characteristic of the lignone complex strictly speaking, or (*b*) of by-products.

We have previously shown (*Journ. Chem. Soc.*, 1899, lxxv., 752) shown that the latter hypothesis is probable as regards the colour reaction with phloroglucol and other phenols, and have given some evidence for ascribing them to the presence of hydroxy-furfurals in the ligno-celluloses. Compounds of this series appear to be normal by-products of spontaneous changes which they undergo in contact with atmospheric air and moisture. By the present investigation this basis of interpretation is strengthened, and our results lead to the following particular conclusions :—

(a) *Phloroglucol Reactions.*

There is a main reaction as between the ligno-cellulose and the phenol which is quantitative in character and is independent of the colour reactions.

This colour reaction is due to an associated by-product, and represents only the effect of a fraction of the total phenol combining synthetically.

(b) *Reactions with Bases.*

These reactions are not in the same sense quantitative in character, but the degree of reaction is a function of the conditions of reaction, similarly to the reactions of the ligno-celluloses in combining with colouring matters.

Incidentally, we have devised experimental methods which will be found to facilitate the investigation of the constitutional problems presented by this group of "natural" products.

Interaction of Phloroglucol and Ligno-cellulose.

The general character of this reaction is shown by the following comparative experiments :—

Equal quantities of mechanical wood pulp were treated—(1) with 1 per cent of the phenol : (2) with 10 per cent of the phenol in presence of hydrochloric acid (10 per cent HCl).

After sixteen hours' digestion, the products were examined :—In (1) the phloroglucol was entirely removed from the solution ; in (2) the phenol was in excess. Notwithstanding this, the intensity of colour development was stronger in 1 than in 2.

After washing exhaustively, drying, and weighing, the excess of weight of 2 over 1 was found to be 3·5 per cent, due to the further combination with the phenol ; therefore the total weight of phloroglucol taken up in combination was 4·5 per cent, neglecting the water split off in reaction.

The following conclusions may be drawn from the observations :—There are two reactions, (*a*) with the production of a coloured body—the limit of this reaction is reached with a proportion of the phenol less than 1 per cent of the ligno-cellulose ; (*b*) a further combination with the phenol to form a compound which resists washing with water.

* Original communicated to the *Berichte*.

In order to determine the maximum absorption of the phenol, we have adapted the well-known reactions of phloroglucol with furfural in the presence of 12 per cent hydrochloric acid to a simple volumetric method, using standard test solutions of concentration 0·4 to 0·5 per cent, and carrying out the reactions at 70° C.

We find that mechanical wood pulp is a very sensitive indicator, being visibly stained by phloroglucol in solution of 1 to 30,000.

In the details of this method we have taken advantage of the exhaustive research of E. Kröber in the *Journ. Landwirthschaft* (1901, p. 379).

As this method will be found of interest in technical investigations, we are communicating a special descriptive note to a technical journal (*Chemiker Zeitung*, xxxi., 725). It is sufficient to note here that it enabled us rapidly to estimate the phenol within the limits 0·5 per cent of the quantity used in our experiments.

Employing this method we avoid larger errors due to the losses of weight of the ligno-celluloses under treatment with the reagents, followed by exhaustive washing, and we are able to determine the actual maximum absorption of the phenol from solution. The following numbers have been determined :—

	Maximum absorption of phloroglucol. Per cent of Faserstoff.
Mechanical wood pulp	6·71, 6·63,
Jute	4·23, 4·20, 4·34
Wood cellulose (sulphite) ..	0·75
Esparto cellulose	0·50
Cotton cellulose	0·20

On the basis of these numbers it is clear that a quantitative technical method for the estimation of mechanical wood pulp in papers is provided, which is free from the errors inevitably associated with a colorimetric process. But the method is also of use in investigating constitutional problems ; thus we may cite observations upon two derivatives of a well characterised ligno-cellulose, the jute fibre substance, as under :—

	Absorption of phloroglucol. Per cent derivative.	Per cent original.
Jute, fully chlorinated (by combination with 8 per cent Cl)	3·9	4·0
Jute, acetylated (to 29 per cent increase of weight)	3·5	4·54

(No colour reaction in either case).

We infer from these results that chlorination produces no important change of constitution in the lignone complex, nor does the process of acetylation. But the disappearance of the colour reaction is in accordance with the view that this is due to a by-product of the *furfural* series which would react with the acetyl residue by its aldehydic CO group.

The evidence so far obtained goes to show that the main reaction with phloroglucol is, in fact, a reaction of synthesis with the typical quininoid groups of the lignone. It is important to note that it bears no relation to the proportion of furfural-yielding constituents of the ligno-cellulose.

In relation to the groups of celluloses and their differences the numbers obtained for esparto and wood cellulose would be influenced by residues of the lignone constituents.

Since by hydrolysis the celluloses are partially resolved with liberation of aldehydic CO groups, measured by cupric reduction methods (C. G. Schwalbe, *Ber.*, 1907, xl., 1347), we included two typical extreme "hydro-celluloses" prepared by the action of HCl (gas), as below.

	Maximum absorption of phloroglucol
Hydro-cellulose (cotton)	0·42
Hydroligno-cellulose (jute)	4·45

The increases over the normal thus resulting have no relation to the very large increase of the free aldehydic CO groups.

It should be noted in reference to this point that the CO groups of the sugar aldehydes require a different set of conditions for reaction with productiou of insoluble products of condensation (C. Councler, *Ber.*, xxviii., 24).

Reactions of Bases with Ligno-cellulose.

Aniline and its homologues give well-marked colour reactions with the ligno-celluloses. These reactions are modified by the introduction of negative substituting groups; thus, the nitranilines give deep red colorations, and *p*-nitraniline has recently been proposed as giving more characteristic reactions (Wheeler, *Ber.*, 1907, 1888).

With the diamines there are equally characteristic colorations, and the best known of these reactions is that obtained with dimethyl-*p*-phenylenediamine. Wurster in his original papers refers the reaction to the active oxygen present in ligno-celluloses (*Ber.*, xix., 3217; xx., 808). It is evident that this effect is one of several factors of a complex result, as, indeed, has been recognised by Wurster in later publications (*Journ. Soc. Chem. Ind.*, 1903, xxii., 824).

We have made a quantitative examination of the reaction with the dimethyl base to determine its general character, making observations on the depth of colour developed in combination.

Four quantities of pine-wood meal, 1 grm. each air-dry, were treated with 0·005, 0·01, 0·02, and 0·05 grm. respectively, of dimethyl-*p*-phenylenediamine hydrochloride, each portion being dissolved in 20 cc. of 5 per cent sodium acetate solution. A fifth portion of 1 grm. was included in the series as a blank, since the woods retain nitrogenous constituents. The intensity of the colour was proportional to the quantity of base employed.

After sixteen hours, all the liquids still contained excess of the base, and gave a reaction with ligno-cellulose proportional to the quantity of base originally employed.

The product was thoroughly washed with water, and the nitrogen in the coloured product was estimated without previous drying.

The following numbers were determined, deducting in each case the nitrogen estimated in the "blank":—

Percentage of hydrochloride taken per cent of ligno-cellulose.	Nitrogen fixed in combination, per cent.	Equivalent of dimethyl-*p*-phenylenediamine.
0·5	0·028	0·14
1·0	0·056	0·28
2·0	0·112	0·56
5·0	0·490	2·45

These percentages, if calculated to the anhydrous ligno-cellulose, must be increased in the ratio 90 : 100.

From these results it appears that the reactions of the ligno-celluloses with these bases are not, in the first instance, reactions with the ligno-cellulose proper; but with the aldehydic by-products or groups tending to assume the aldehydic configuration.

The quantitative features of the reactions are those which obtain rather in dyeing processes; that is, the baths are not exhausted, and the final distribution of the base, as between the ligno-celluloses and the solution, represents an equilibrium determined in part by concentration and attendant physical conditions.

Phenylhydrazine.

The reactions with this base are of the same general character, but in the first instance there is a complete absorption by combination. This is illustrated by the following numbers:—

Phenylhydrazine taken per cent of ligno-cellulose.	Phenylhydrazine absorbed.
0·5	0·5
1·0	0·9
2·0	1·6
5·0	2·5

The aldehydic constituents involved in these reactions appear to be the same as those which react with phloroglucin with development of colour.

In confirmation of this the ligno-cellulose after treatment with phenylhydrazine give no colour reaction with phloroglucin until after prolonged digestion with the acid solution of the phenol, and as a result of the gradual decomposition of the hydrazone.

It may be mentioned, though evident *à priori*, that the products of synthesis with phenylhydrazine, presumably hydrazones, are more resistant than the compounds with monamine and diamine bases, which are readily resolved by hydrolytic agents, acid and basic; the phloroglucides, on the other hand, are very resistant. They are not resolved by boiling with dilute alkalis.

This is in accordance with the quantitative relations disclosed by our results.

Hydroxylamine.

The ligno-celluloses react with this base with change of colour, which may be generally described as a partial bleaching.

We have not yet investigated those reactions quantitatively, but we may record the observation that their combination with this base entirely prevents the colour reactions with aniline and the diamines.

The reaction with phloroglucol is retarded, but after a period of digestion with the acid reagent the characteristic full development of colour is obtained.

It is evident, therefore, that the phloroglucides are well characterised derivatives, and enable us to fix the more reactive groups of the lignone complex; we hope thereby to be able to study certain decompositions into proximate products without the complications which have hitherto rendered this a matter of exceptional difficulty.

In a later communication we shall give the results of our further investigations of the constitution of the ligno-celluloses.

THE

BALANCING OF IONIC CHEMICAL EQUATIONS.

By WILLIAM JAY KARSLAKE.

CHEMICAL processes can be written in the form of equations in which substances are represented by their chemical symbols and formulæ. The balancing of a chemical equation then consists in finding those numerical factors called coefficients, by which each symbol and formula must be multiplied in order that the proper proportions will be expressed between the various initial and final substances involved in the change.

In making out chemical equations considerable trouble is sometimes experienced in determining the exact coefficients to be used, and therefore various devices and methods for balancing them have come into use. The principal methods for balancing ordinary chemical equations are:—

1. *The Tentative or Trial Method*, which consists in inspecting the equation and trying various coefficients until the proper ones are found.

2. *The Partial Equation Method*, which is an arithmetical device whereby the final equation is obtained through the summation of a series of partial equations.

3. *The Dualistic or Anhydride Method*, a relic of the old dualistic system of Berzelius, in which all oxygen compounds are written in the form of a positive and a negative part, as a basic and acidic oxide, and it is these various parts which are regarded as undergoing chemical change.

4. *The Algebraic Method* (James Bottomley, CHEMICAL NEWS, 1878, xxxvii., 110), wherein the method of indeterminate coefficients is applied, and the numerical value of the coefficients found by solving a set of simultaneous equations.

5. *The Hydride Hydroxide Method* (Ostwald's "Principles of Inorganic Chemistry," translated by Alex. Findlay,

2nd Edition, p. 607), whereby the coefficients are obtained by regarding the interacting substances as derived from those particular hydrides and hydroxides obtained by adding the elements of water to certain hydrogen and oxygen compounds of the substances under consideration.

6. *The Method of Positive and Negative Bonds* (O. C. Johnson, Chemical News, 1880, xlii., 51; Prescott and Johnson, "Qualitative Chemical Analysis," 5th Edition, p. 238), according to which "the number of bonds changed in one molecule of each shows the number of molecules of the other which must be taken, the words 'each' and 'other' referring to the oxidising and reducing agents" which are mutually interacting upon each other. The term "bond" as here used represents the unit of valence *actively* exhibited by the element at the time of consideration, and is counted as a relatively positive or negative quantity according to circumstances.

While some of these methods are of value for the solution of ordinary empirical equations, most of them fail to furnish the means of solving an equation when written in the ionic or partly ionic form. This failure arises in part from the fact that in many cases the electrical charges on the ions are not accounted for, and any ionic equation to be correct must be so written that the interacting system is shown to remain electrically neutral; that is, equal quantities of positive and negative electricity must simultaneously appear or disappear in such a manner that there is no change in the sum total of the electrical charges in the system. The correct weight-ratios, therefore, between the initial and final substances involved in any ionic chemical change can only be had—(1) when the law of the conservation of weight holds good, as in ordinary equations; and (2) when the algebraic sum of the initial electrical charges is equal to that of the final electrical charges.

Aside from the tentative or trial method and the method of obtaining them from their corresponding empirical equations, there seems to be no recorded method to serve, as a rule, for the systematic balancing of ionic equations (see Talbot and Blanchard, "The Electrolytic Dissociation Theory," Chapter IV.). Yet the so-called "bond method" cited above may be extended so as to serve quite as well for the balancing of ionic equations as it does for empirical equations. To this end it is only necessary (1) to include the term "ion" under that of "molecule"; (2) to observe that while the sum of the positive and negative bonds of the atoms forming a *molecule* is zero, the sum of those forming an *ion* is equal to the valence of that ion as expressed by the number and sign of its electrical charges; (3) to count hydrogen in chemical combination as always possessing one positive bond, oxygen as possessing two negative bonds, and free elements as having no bonds; and (4) to bear in mind the necessary condition of electrical neutrality which holds for all ionic changes. As thus extended the rule for balancing ionic, partly ionic, or empirical equations may be stated as follows:—(1) The number of bonds changed in one molecule or ion of the substance oxidised shows the number of molecules or ions of the substance reduced, and *vice versâ*; and (2) the difference between the algebraic sum of the initial and final electrical charges of the partially balanced equation shows the number of molecules or ions of the remaining substances entering into the reaction, if any, which must be taken.

A few equations will illustrate the application of the method as thus extended. Reactions typical of the various kinds of ionic chemical processes in oxidation and reduction will be selected.

$$5Fe^{\cdot\cdot} + MnO_4' + 8H^{\cdot} = 5Fe^{\cdot\cdot\cdot} + Mn^{\cdot\cdot} + 4H_2O \quad . \quad . \quad 1.$$

This equation expresses the oxidation of diferrion, $Fe^{\cdot\cdot}$, by permanganion, MnO_4', in the presence of hydrion, $H^{\cdot}$. (For the system of ionic nomenclature, see James Walker, Chemical News, 1901, lxxxiv., 162). Here the iron in one molecule of diferrion, $Fe^{\cdot\cdot}$, gains one positive bond in passing to triferrion, $Fe^{\cdot\cdot\cdot}$; hence the number of molecules of permanganion, MnO_4', which must be taken is 1. And since all of the manganese in permanganion passes to dimanganesion, $Mn^{\cdot\cdot}$, the latter must also have a coefficient of 1. Again, since the four oxygen atoms in one molecule of permanganion, MnO_4', have a total of eight negative bonds, the manganese must have seven positive bonds, of which five are lost in passing to dimanganesion, $Mn^{\cdot\cdot}$. Hence, five molecules of diferrion are oxidised to the corresponding number of molecules of triferrion. Further, the algebraic sum of the ionic electrical charges in the final system is +17; therefore hydrion, $H^{\cdot}$, must be given a coefficient of 8 in order that the sum of the total ionic charges in the initial system be the same. From this it follows that the water formed has a coefficient of 4.

$$Cr_2O_7'' + 6I' + 14H^{\cdot} = 2Cr^{\cdot\cdot\cdot} + 3I_2 + 7H_2O \quad . \quad . \quad 2.$$

This equation represents the reduction of dichromanion, Cr_2O_7'', by iodidion, I', in the presence of hydrion, $H^{\cdot}$. The total chromium in one molecule of dichromanion has twelve positive bonds, and it loses six of them in passing to trichromion, $2Cr^{\cdot\cdot\cdot}$. Hence, six molecules of iodidion are oxidised to three molecules of free iodine when written as in the equation. On the other hand, the iodine in one molecule of iodidion, I', in passing to the form of free iodine, I, loses only one negative bond, which is equivalent to gaining one positive bond, and, consequently, the coefficient of the dichromanion is 1 and that of the trichromion formed is 2. The algebraic sum of the electric charges in the final system, the water and the free iodine being neutral, is +6, and in order that the initial system may have the same electrical content the coefficient of the hydrion, $H^{\cdot}$, must be 14. Hence, the water formed has a coefficient of 7.

$$2SO_3'' + 2Br_2 + 2H_2O = 2SO_4'' + 4Br' + 4H^{\cdot} \quad . \quad . \quad 3.$$

This equation represents the oxidation of sulphosion, SO_3'', to sulphanion, SO_4'', by means of bromine water. The sulphur in the sulphosion in passing to that in the sulphanion gains two positive bonds, thus reducing two molecules of free bromine to form, as written, four molecules of bromidion, Br'. The total bromine in one molecule of free bromine, Br_2, gains two negative bonds, which is equivalent to losing two positive bonds, and, consequently, 2 is the coefficient of the sulphosion which is oxidised. Further, since the sum of the ionic electrical charges in the initial system is −4, bromine and water being neutral, it follows that the hydrion, $H^{\cdot}$, formed in the final system, must have a coefficient of 4, and from this the water in the initial system must have a coefficient of 2.

$$2Fe^{\cdot\cdot\cdot} + Sn^{\cdot\cdot} = 2Fe^{\cdot\cdot} + Sn^{\cdot\cdot\cdot\cdot} \quad . \quad . \quad . \quad . \quad . \quad 4.$$

This equation represents the interaction of triferrion, $Fe^{\cdot\cdot\cdot}$, and distannion, $Sn^{\cdot\cdot}$, to form diferrion, $Fe^{\cdot\cdot}$, and tetrastannion, $Sn^{\cdot\cdot\cdot\cdot}$. Here the iron in passing from triferrion to diferrion loses one positive bond, while the tin in passing from distannion to tetrastannion gains two bonds. This gives 1 for the coefficient of the distannion and 2 for that of the triferrion. The coefficients of the products formed are evident. This type of reaction illustrates the reduction or oxidation of one simple ion by another.

$$3Cu + 8H^{\cdot} + 2NO_3' = 3Cu^{\cdot\cdot} + 2NO + 4H_2O \quad . \quad . \quad 5.$$

This equation represents the action of dilute nitric acid upon metallic copper. The free copper is oxidised to dicuprion, $Cu^{\cdot\cdot}$, thus gaining two positive bonds; hence, 2 is the coefficient of the nitranion, NO_3'. On the other hand, the nitrogen in one molecule of the nitranion in passing to the form of nitric oxide loses three positive bonds; hence, three molecules of metallic copper are oxidised. Since the sum of the ionic electrical charges of the final system is +6 it follows that 8 must be the coefficient of the hydrion, $H^{\cdot}$, in order that the initial system may have the proper number of charges. Since all of the hydrion passes to the form of water the coefficient of the water formed must be 4.

$$Zn + 2H^{\cdot} = Zn^{\cdot\cdot} + H_2 \quad . \quad . \quad . \quad . \quad . \quad 6.$$

This equation represents the action of hydrion upon metallic zinc. It is an oxidation and reduction reaction, the zinc gaining two bonds in being oxidised to zincion, $Zn^{\cdot\cdot}$, while the hydrion loses one bond in being reduced to free hydrogen. Hence the coefficients are 2 and 1 as written. This reaction is typical of the preparation of hydrogen by the action of acids upon metals in general. It is also typical of the oxidation and reduction of many free substances by ionic substances, such as, for example, the precipitation of metallic copper from aqueous solutions of its salts by means of metallic zinc, $Cu^{\cdot\cdot} + Zn = Cu + Zn^{\cdot\cdot}$, or the liberation of bromine from aqueous solutions of bromides by means of free chlorine, $2Br' + Cl_2 = Br_2 + 2Cl'$, &c.

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INCANDESCENT ILLUMINANTS.*

By JAMES SWINBURNE, F.R.S., &c.

A LITTLE more than twenty years ago, Auer von Welsbach, who was engaged on researches on the rare earths, invented the modern incandescent mantle. His first mantles were made of zirconia and yttrite earth, in the proportion to make a normal zirconate. Shortly afterwards, he found that the best material has a basis of thoria. Pure thoria, which requires care in its preparation, gives very little light, but if a small percentage of a coloured and permanent oxide, such as ceria, is added, it gives good illumination.

There has been much discussion about the theory of the incandescent mantle. It has been generally assumed that the temperature of a Bunsen burner is too low for a mantle to give the light it does by simple radiation, unless it is much hotter than the flame. Unfortunately, the temperature of the flame is generally taken with a thermo-couple, and this gives far too low a reading, as the thermo-couple never reaches the real temperature of the flame. But, admitting that the temperature of the flame is high, it is still urged that the light given by the thoria with a small percentage of ceria is so great that there is something else than mere thermal radiation. It is said that the ceria acts as a catalytic agent, and that it oscillates between two states of oxidation. Ceria does act in somewhat the same way as platinum; for instance, if a ceria mantle is put on a lighted burner, and the burner turned out, and the gas turned on again, the ceria mantle will glow and will finally light the gas. It is odd that this is not brought forward by the advocates of the catalysis theory; but the opponents might urge that zirconia will do the same thing, and the zirconia mantle gives very little light. This does not really dispose of the catalytic theory.

According to the simple radiation theory, the light depends only on the emissivity, or blackness of the mantle, and its temperature. Its temperature must be lower than the flame, as it must be robbing the flame of the heat it radiates. In order to give the flame every chance of supplying the heat, the threads of the mantle have to be made very fine, so that the flame can rush through the meshes, and the hot gas should be in brisk movement through the interstices of the mantle. By using a special draught arrangement, known as the intensive system, about twice the light per cubic foot of gas can be obtained. In order to get the highest temperature the emissivity should be low, that is to say, the mantle should be very white; but then, though it would get to a high temperature, it would give very little light. On increasing the emissivity the light will first increase, but this means a lower temperature, so that as the emissivity is increased from white to black, the total radiation increases, but as that means a greater abstraction of heat from the flame, the mantle is cooler, and therefore radiates a larger proportion of the energy as heat and a smaller proportion as light, so the mantle gets redder and gives less light. This is just what happens in practice, whether ceria or any other coloured oxide is used.

It has been urged that as pure ceria is white, adding it cannot make the mantle blacker; but ceria is white only when cold. A mantle may look quite white cold, and be darker in colour when hot. Rubens has devised an experiment to show this. The mantle is strongly illuminated by an arc and condenser, and its image is thrown on the screen. It looks quite white, of course. On lighting the gas, the mantle, instead of becoming still brighter, at once becomes dull. Again, alumina, which is white, gives little light. Chromium oxide is so dark that it gives only a dull red glow. But on adding a little chromium oxide to the alumina, a dark red light is first given, because the chromium oxide is too dark; but as soon as it combines with the alumina to make a light pink mantle, a good light is obtained.

The incandescent mantle is now applied not only to the ordinary Bunsen burner, but to an inverted form, which lends itself to decoration, and to the petroleum lamp. It is now also applied to air carrying a little hydrocarbon gas, and this application is said to provide an extraordinarily cheap light, which is especially useful for country houses.

One of the drawbacks of gas, compared with electric lighting, is that merely turning on does not light gas. This difficulty has been largely overcome by the use of the by-pass, but further advances have been made. Welsbach has discovered that an alloy of cerium and iron gives off sparks on being scraped or filed, and a burner has been designed in which the act of turning on the gas scrapes a little wheel of this alloy, causing a spark, which lights the gas. This overcomes the drawback of having a little jet always burning. Another invention allows the gas to be lighted from a main tap. Each burner has an attachment, which lets the gas straight through to the burner when the pressure is on; but on turning the main supply off, and allowing a little gas to pass at the controlling tap, the attachment to each burner turns off the burner and lights a little pilot jet, which keeps alight until the light is wanted again. On turning on the main tap, the pilot jets light the various burners and go out themselves. By this means burners can be fully lighted up by turning one tap at the door of the room.

The electric incandescent light is undergoing a great change. Carbon is being replaced by metal wires. It has been found possible to make wires of high enough resistance of tungsten, osmium, tantalum, and a few other metals and compounds. The osmium lamp was the first of these, but there was difficulty in making it of high enough resistance. The tantalum lamp is now in great demand. It is made for 100 to 130 volts, and is much more efficient than the carbon lamp. It will not last long on alternating currents, however. The wires of a lamp that have been run for some time on a direct current show a curious notched or crinkled appearance under the microscope. But a wire that has been run on an alternating circuit looks as if the metal had been melted into short cylinders with round ends, and these cylinders had stuck together end to end without their centres being in a line. Sometimes the little cylinders are nearly separated, merely touching at a corner. This action is very extraordinary, and has never been explained. In addition to this, when a lamp breaks down on an alternating circuit, the wire sometimes goes at one point, and sometimes it breaks in several places, and tangles itself up in an extraordinary way; at other times it breaks up into numerous little pieces, which will be found lying on the inside of the globe. Some of the other lamps show a change under the action of the current, but it is not so marked as in the case of tantalum.

One of the most interesting of the new lamps is the Zircon. It is said to be made of zirconium and tungsten, and lamps of this material have been made for 200 volts, a matter of the greatest importance from a distribution point of view. It is possible that the conductor is really a

* Abstract of a Discourse delivered at the Royal Institution, April 26, 1907.

zirconide of tungsten, and this opens up a new series of compounds. A Zircon lamp for 100 volts has really six separate loops of wire mounted in series inside a bulb. A recent improvement is to provide an extremely light spring for each loop, so as to keep it taut. The lamp can then be used in any position.

Tungsten seems to be the favourite metal, as it gives a very high efficiency. It is probable the lamp of the future will have an efficiency of nearly a candle per watt, and this is promised by the use of tungsten. At the same time it must be admitted that to make a wire with a resistance of 500 ohms small enough to give 20 candles with 20 watts is a triumph of inventive skill.

The lecture was illustrated by numerous experiments.

THE USE OF SUCCINIC ACID AS A STANDARD IN ALKALIMETRY AND ACIDIMETRY.

By I. K. PHELPS and J. L. HUBBARD.

SUCCINIC acid as a standard in alkalimetry and acidimetry has had an extended use for some time. We are not aware that the best methods of preparation of pure material for such a purpose, or the limits of accuracy of succinic acid in such a procedure, have been recorded. We give in detail below work concerning these points.

To determine the strength of the solution of ammonium hydroxide used in this work in neutralising definite weights of succinic acid, a solution of hydrochloric acid approximately *n*/10, was made up by diluting in the usual way with distilled water pure hydrochloric acid. The solution of hydrochloric acid was standardised by precipitating in a volume of 250 cc. definite portions of it held in a platinum dish with silver nitrate in excess in presence of a few drops of nitric acid, filtering off the precipitate, allowed to stand twenty-four hours, after cooling to zero centigrade to remove from solution traces of silver chloride (W. A. Roth, *Zeit. f. Angew. Chem.*, xvii., 716), filtering off on asbestos under pressure in a perforated platinum crucible, rinsing with water cooled to zero, drying at 100° C., and weighing after cooling in a desiccator. The solution of ammonium hydroxide was titrated against the solution of hydrochloric acid, using tincture of cochineal as the indicator, and by diluting with distilled water in suitable amounts was made of such strength that 1 cc. corresponded exactly to 1 cc. of the hydrochloric acid solution.

Succinic acid was prepared in four dfferent ways—by the hydrolysis of the pure ester, by hydration of the pure anhydride, by crystallisation of the acid from a solution of the succinic acid of commerce in hot water, and by crystallisation of the acid from the solution of the acid of commerce in hot water containing nitric acid.

From purified succinic ester, boiling at 213·3—213·5° C. under a barometric pressure of 749 mm., pure succinic acid was obtained by boiling it for four hours on a return condenser with nitric acid and water in these proportions—20 cc. of succinic ester, 200 cc. of water, three drops of nitric acid. This solution was evaporated to crystallisation, and, after filtering off from the mother-liquor, the solid product was re-crystallised from distilled water. These crystals were dried carefully in the open air to constant weight, and it was found that on standing over sulphuric acid in a desiccator this weight remained unchanged. By this procedure the purest succinic acid melting in an open capillary tube at 182·3° C. was obtained.

For the preparation of the acid from succinic anhydride the anhydride was purified by re-crystallising from absolute alcohol until the crystals obtained after carefully drying melted sharply at 119° C. The pure anhydride obtained in this manner was converted to the acid by dissolving it in distilled water heated to the boiling-point, filtering off the crystals formed on cooling the solution, and drying. It was found that these crystals, as in the case of the succinic acid crystals described above, came to constant weight when dried in the air, and that this weight remained unchanged when the product was allowed to stand in a desiccator over sulphuric acid. Samples made in this way melted at 182·8° C. in an open capilliary tube.

Preparations of succinic acid were made from the acid of commerce by dissolving the latter in distilled water at the boiling-point, crystallising by cooling and drying in the air. No loss in weight was found when the air-dried material was exposed in the desiccator. It melted in an open capillary tube at 181·7° C.

The acid was also made by dissolving the succinic acid of commerce in boiling water, adding nitric acid, crystallising, and drying the crystals thus obtained. In this manner a product of a slightly higher degree of purity was obtained than that crystallised from water. This product melted in an open capilliary tube 182·3° C.

TABLE I.

No.	Succinic acid.	HCl corresponding to succinic acid— Found.	Theory.	Error.
	Grm.	Grm.	Grm.	Grm.
1.	0·2000	0·1231	0·1235	0·0004 –
2.	0·2000	0·1231	0·1235	0·0004 –
3.	0·2000	0·1231	0·1235	0·0004 –
4.	0·2000	0·1231	0·1235	0·0004 –
5.	0·2000	0·1231	0·1235	0·0004 –
6.	0·2000	0·1231	0·1235	0·0004 –
7.	0·2000	0·1233	0·1235	0·0002 –
8.	0·2000	0·1233	0·1235	0·0002 –
9.	0·2000	0·1231	0·1235	0·0004 –
10.	0·2000	0·1233	0·1235	0·0002 –
11.	0·2000	0·1234	0·1235	0·0001 –
12.	0·2000	0·1234	0·1235	0·0001 –
13.	0·2000	0·1235	0·1235	0·0000
14.	0·2000	0·1235	0·1235	0·0000
15.	0·2000	0·1235	0·1235	0·0000
16.	0·2000	0·1235	0·1235	0·0000

In all of the experiments recorded in the table *definite* portions of succinic acid were dissolved in distilled water, and into the solution the ammonium hydroxide of definite strength was drawn carefully from a burette until the succinic acid was exactly neutralised as shown by the cochineal tincture used to indicate the completion of the reaction. The experiments were conducted so that the final volume in each case was about 250 cc. at the completion of neutralisation of the succinic acid. The succinic acid used in Experiments 1, 2, 3, and 4 recorded in the table was that obtained by crystallising the succinic acid of commerce from water at the boiling-point, and dried in the air. The material in 5 and 6 was the same product crystallised from water, and dried in a desiccator. In Experiments 7 and 8 the succinic acid used was that purified by crystallising from hot water with a few drops of nitric acid. In Experiments 9, 10, 11, and 12 the succinic acid used was made from the purified anhydride, dried to constant weight in the air. The material used in Experiments 13, 14, 15, and 16 was the succinic acid prepared by hydrolysing the pure succinic ester boiling at 213·3—213·5° C.

It is clear from the work shown in the table that succinic acid may serve admirably as a standard for work in alkalimetry and acidimetry. It is further obvious that for such work succinic acid of a fair degree of purity may be prepared by crystallising the acid of commerce from water at the boiling-point, or preferably by crystallising from water at the boiling-point containing nitric acid. The product obtained by the hydration of the anhydride is of an excellent state of purity. Succinic acid of ideal constitution may be prepared by hydrolysing the pure ester. While in every case air drying of the samples is sufficient, drying in a desiccator over sulphuric acid involves no risk of the formation of the anhydride.

Since succinic ester in a state of purity may be prepared with ease, succinic acid is conveniently available as a standard in alkalimetry and acidimetry. It is equally reliable with the previously most valued standard—hydrochloric acid standardised gravimetrically as silver chloride. —*American Journal of Science*, xxiii., p. 211.

SOME ASTRONIMICAL CONSEQUENCES OF THE PRESSURE OF LIGHT.*

By Professor J. H. POYNTING, Sc.D. F.R.S.

THE experiments of Lebedew and Nichols and Hull have proved conclusively that light presses against any surface upon which it falls, and the extraordinarily accurate experiments of Nichols and Hull have fully confirmed Maxwell's calculation that the pressure per square centimetre is equal to the energy in the beam per cubic centimetre.

A clearer idea of the effect of light or radiation pressure is obtained by thinking of a beam of light as a carrier of momentum. We then see that not only does it press against a receiving surface, but also against the surface from which it started.

Some experiments by Dr. Barlow and myself appear to bring to the front this conception of light as a momentum carrier. If a beam falls on a black surface at an angle to the normal, there should be a tangential stress along the surface. An experiment was described in which light fell on a blackened disc at the end of a torsion arm, the disc being at right angles to the arm (*Phil. Mag.*, 1905, ix., p. 169). The disc was pushed round by the tangential stress. The experiment was carried out in a partially exhausted vessel, but the residual air was a source of disturbance by convection and radiometer effects. A better experiment was made by suspending a disc of mica blackened beneath, about 2 inches in diameter by a quartz fibre, the disc being horizontal and suspended from its centre. When a beam of light fell at 45° on a part of the disc, the horizontal component of the beam being at right angles to the radius to the part where it fell, the disc moved round through the combined effects of convection, radiometer action, and the tangential stress. When the beam was allowed to fall on the same place at 45° on the other side of the vertical, convection and radiometer action were very nearly as before, but the tangential stress was reversed. The difference in torsion in the two cases was twice that due to the tangential stress. An experiment with prisms (*Ibid.*, p. 404) was also described.

Regarding a beam of light as a momentum carrier, it is easily seen that if the receiving surface has velocity u towards the source and the velocity of light is U, the pressure is increased by the motion by the fraction u/U. If the velocity is reversed, the pressure is decreased by this fraction. This is the "Doppler reception effect."

If the source is moving, and we assume that the amplitude of the emitted waves depends on the temperature and nature of the source alone, it can be shown that the pressure on the source is $U/U \pm u$ of its value when the source is at rest. This is the "Doppler emission effect."

In considering the consequence of light pressure, it is necessary to know the temperature of a body exposed to the sun's radiation. It can be shown that a small black particle, at the distance of the earth from the sun, has about the mean temperature of the earth's surface, say 300° Abs., and that the temperature of the sun is about twenty times as high, say 6000° Abs. The temperature of the particle varies inversely as the square root of its distance from the sun.

The direct pressure of sunlight is virtually a lessening of the sun's gravitation pull. On bodies of large size this is negligible. On the earth it is only about a forty-billionth of the sun's pull, but the ratio increases as the diameter decreases, and a particle one forty-billionth of the earth's diameter, and of the same density, would be pushed back as much as it is pulled in, if the law held good down to such a size. If the radiating body is diminished, the ratio of gravitation pull to light push is similarly diminished, and it can be shown that two bodies of the temperature of the earth's surface and of the earth's mean density would neither attract nor repel each other, if their diameter was about 1 inch. The consequence of this on a swarm of meteorites is obvious. It is probable that this balancing of gravitation and light pressure must be taken into account in the motion of the particles supposed to constitute Saturn's rings.

When we consider the motion of a small particle round the sun, we have, first, the direct pressure lessening gravitation. If it has density equal to that of the earth and diameter 1/1000 inch, the lessened pull at the distance of the earth will imply a lengthening of the year by nearly two days. Secondly, the Doppler emission effect comes into play, for the particle crowds forward on its own waves emitted in front, and draws away from those emitted behind, so that there is increase of pressure in front and a decrease behind. Thus there is a force resisting the motion. The particle will then tend to fall inwards in its orbit, and in the case considered about 800 miles in the first year. It would probably move in a spiral into the sun, and reach it in less than 100,000 years. A particle 1 inch in diameter would reach the sun from the earth in less than a hundred million years. The Doppler reception effect will not come into play in a circular orbit, but in an elliptic orbit it acts as if it were a force resisting change of distance, and therefore it tends to make an elliptic orbit even more circular.

Applying these considerations to a comet regarded as a swarm of small particles coming into our system, a sorting action will at once begin. The smaller particles will have their period of revolution lengthened out more than the larger ones, and they will tend to trail behind. The Doppler emission effect will damp down the motion, and again, more markedly with the smaller particles, and all will tend to spiral into the sun. The Doppler reception effect will tend to destroy the ellipticity of the orbit, more especially with the smaller particles, and ultimately the particles of different sizes may move in orbits so different that they may not appear to belong to the same system. In course of time they should all end in the sun. Perhaps the zodiacal light is due to the dust of long dead comets.

It appears just possible that Saturn's rings may be cometary matter which the planet has captured, and on which these actions have been at play for so long that the orbits have become circular.

* Abstract of a Discourse delivered at the Royal Institution, May 11, 1906.

NOTICES OF BOOKS.

Investigations of the Theory of the Photographic Process. By S. E. SHEPPARD, D.Sc. (Lond.), and C. E. KENNETH MEES, D.Sc. (Lond.). London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1907.

THE authors of this discussion of the theory of the photographic process have applied physico-chemical methods to the study of development, fixation, &c., and have to record some important results thereby obtained. They have, as far as possible, performed all experiments quantitatively, and the numerical results are in all cases given in full, while the references to authoritative text-books and original articles, and the short historical accounts of each division of the subject, show that they have made every endeavour to provide as comprehensive a view of the whole theory of photographic work as possible. In the chapters on the sensitometry of photographic plates an attempt is made to add to the value of the plate as an instrument of research by determining the relation between the light employed

and the effect produced, and a short account is given of the colour sensitiveness of plates; this last chapter having been left unaltered since it was written now over a year ago, the latest work that has been done by Callier and by Belin on the subject could not be described, but the authors have evidently devised reliable methods of investigating an important question from a quantitative point of view.

A Text-book of Electro-chemistry. By MAX LE BLANC. Translated by WILLIS R. WHITNEY, Ph.D., and JOHN W. BROWN, Ph.D. New York: The Macmillan Company. London: Macmillan and Co., Ltd. 1907.

THE new translation from the fourth German edition of this text-book constitutes the second English edition, in which, although the earlier version has been freely used, many important additions and alterations have been made. A new feature is the adoption of a consistent notation throughout the book; in it the various symbols are used as far as possible in the same sense as in other important works on physical and electro-chemistry, and although its use will perhaps be found a little troublesome at first, the student working systematically through the book will no doubt very soon get accustomed to it, while the reader, who is merely referring to the book for special information, will in many cases understand it readily if he is acquainted with chemical or electrical literature, and it is explained in full in an appendix. The text-book has been much used in England, and no doubt the new edition will be well received. It gives on the whole a satisfactory survey of theoretical and general electro-chemistry, though in some respects the author's treatment of important branches of the subject is rather scanty. For instance, the relation between chemical constitution and conductivity might with advantage be considered more fully, while the importance of Lorenz's work on the conduction of fused salts would warrant more than an allusion to it in a foot-note only, more especially as much research work on the subject is waiting to be done.

The Chemistry and Technology of Mixed Paints. By MAXIMILLIAN TOCH. New York: D. Van Nostrand Company. London: Crosby Lockwood and Son. 1907.

THIS book is original in conception and working out, and brings before the reader some fresh aspects of the chemistry of paints. It is the first work devoted exclusively to the subject of mixed paints which has yet appeared, and not unnaturally it exhibits the defects which often mar pioneering work, while at the same time it puts new problems before the paint chemist, and opens up a wide field of research. Much of the text is devoted to a description of the author's investigations, and chemists who have had a good general training in analysis will find that many of the author's suggestions for experimental work might, if followed up, lead to important technical developments. In the first part of the book the manufacture of mixed paints is described, with some account of the chemistry of the raw materials, in which the author has omitted much information which is to be found in the usual text-books, and has thus made room for the results of his experiences upon various points of interest or dispute. The chapters on paint vehicles are marked by the same originality and independence of conclusions generally accepted, as shown, for instance, in the section on China Wood Oil, the use of which is frequently condemned, though without due cause in the author's opinion. On the analysis of mixed paints some notes are given, but the subject is not treated sufficiently systematically to make the section of any real use except to an expert already familiar with the general methods employed. In fact the whole character of the book is such that, while it contains much that will be of value as a supplement which throws an interesting light upon recent research, it could not be adopted as a text-book for students who were beginning the study of paint chemistry.

The Textile Fibres. By J. MERRITT MATTHEWS, Ph.D., Second Edition. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1907.

THIS text-book of the physical, microscopical, and chemical properties of the textile fibres is a valuable addition to the literature of the subject, and should be studied from cover to cover by all students of Textile Schools. The author has taken into account the needs of manufacturers, and pays considerable attention to practice, so that the book throws light upon many of the problems which are likely to confront those engaged in the industry. From a scientific point of view the work will be found most stimulating, and as the chemical nature of the fibres has as yet been but little investigated, the worker who uses the book will find that he is not likely to want a profitable subject for research. Many micrographs by the author add to the value of the text, and the laboratory methods used in the qualitative and quantitative analysis of the fibres are fully described, while the comprehensive scheme for the examination of different fibres will be found a valuable practical aid to the student.

Das Werden der Welten. ("The Development of the Worlds"). By SVANTE ARRHENIUS. Translated from the Swedish by L. BAMBERGER. Leipzig: Akademische Verlagsgesellschaft, m.b.H. 1907.

THIS exposition of Prof. Arrhenius's views upon many disputed questions in cosmic physics will receive the careful attention of students of astronomy and of the problems of the cosmos. The fruitfulness of the great Swedish chemist's theories in general chemistry will no doubt influence the minds of many of his readers as to their acceptance of some of his daring assumptions, provided that they are not too rigidly bound by convention, and it goes without saying that he clothes his views in most stimulating language. The central idea of the book is that the world was always essentially the same as it now is, and that matter, energy, and life have only changed form and position in space. Upon this theme he writes with enthusiasm and inspiration, and astronomers and cosmic physicists will find that the book well repays careful study. In particular, emphasis is laid upon the theory of the pressure of radiation, which opens up a wide field of enquiry, and special attention is called to Lebedew's pioneering work, which is generally speaking somewhat neglected. Possibly the parts of the book which will be most interesting to the general reader are those which deal with the appearance of life upon this planet, on which subject the author has some new suggestions to make.

Die Kathodenstrahlen. ("Cathode Rays"). By G. C. SCHMIDT. Braunschweig: Friedrich Vieweg und Sohn. 1907.

THE importance of the possession of an adequate knowledge of the essentials of the electron theory by all who are engaged in scientific work of any description is fully recognised, and this book will consequently receive a hearty welcome on all sides. It contains a clear account of the discovery and properties of the cathode rays, and shows how the electron theory is based upon them. The outlines of the theory are put forward in the simplest possible way, mathematical discussions being omitted as far as possible, and no reader need fear that his scientific knowledge is insufficient to enable him to understand the main purport of the book. Very little previous acquaintance with natural phenomena is assumed; thus the book opens with a chapter on the undulatory theory of light and the nature of the ether, and throughout Prof. Schmidt shows a marked power of insight into the difficulties the new conceptions are likely to present to those who are reading of them for the first time, while his language is admirably suited to dispel these diffi-

culties and to arouse the fullest interest of the reader. The book is divided into short chapters, each of which introduces some new important fact or theory, which is presented in such a way that every advance is thoroughly defined and explored before the next is made, which is a valuable feature from the point of view of the elementary reader.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxliv., No. 25, June 24, 1907.

New Method of Preparing Anhydrous Lithium Oxide.—M. de Forcrand.—Li_2O can be prepared by the dissociation of the carbonate at 780—800° in a current of dry hydrogen, as well as by the dehydration of the hydrate. The author has determined the heat of solution of Li_2O (30 grms.) in 4 litres of water at 15° and obtains the number 31·200 cals., which differs very considerably from that stated by Beketoff. The degree of dilution has a great influence upon the heat of solution, and Li_2O previously dissolved in 4 litres evolves 0·306 cal. when the liquid is diluted to 15 litres. In this respect lithium resembles the metals of the alkaline earths and differs from the alkali metals. The heat of solution also depends upon the temperature, increasing by about 0·098 cal. for every degree.

Hydration of Ethylene Oxides.—Louis Henry.—Epichlorhydrine, $ClCH_2—CH—CH_2$ (O), when subjected to the action of sulphuric acid gives the primary glyceric monochlorhydrine, $ClCH_2—CH(OH)—CH_2(OH)$, and all ethylene compounds containing the group $>C—C<$ (O) resemble it in this respect. This reaction can be employed practically for the preparation of the ethylene glycols, $>C(OH)—C(OH)<$. Thus, if the oxide of isobutylene, $(CH_3)=C—CH_2$ (O), is introduced into water and dilute sulphuric acid is added, heat is evolved, and, after cooling, the glycol can be separated from the liquid by means of potassium carbonate. This glycol is isobutylenic glycol, $(CH_3)_2=C(OH)—CH_2OH$. When oxides richer in carbon are treated in the same way less heat is evolved. Thus oxides containing the group $>C—C<$ (O) differ from the glycolic oxides such as—

$CH_2—(CH_2)_2—CH_2$ (O) or $CH_3—CH—(CH_2)—CH—CH_3$ (O),

which are not affected by sulphuric acid.

Sulphammonium.—P. Lebeau and P. Damoiseau.—In 1905 Ruff and Geisel stated that the action of sulphur upon ammonia may be represented by the reversible equation $10S+16NH_3 \rightleftharpoons N_4S_4+6(NH_4)_2S$, and that the coloration of sulphammonium is produced only in presence of free sulphur, which gives a colloidal solution with the liquefied ammonia. To establish this fact they endeavoured to show the presence of sulphuretted hydrogen and nitrogen sulphide in sulphammonium. However, as a trace of an impurity is often sufficient to bring about a reaction, the authors thought that a trace of water—which is difficult to avoid in the case of a gas as hygroscopic as ammonia—might play some part in the reaction. They therefore repeated the experiments, taking special precautions to ensure the absence of moisture, and then found that Ruff and Geisel's reversible reaction does not represent the true facts unless water is present; and, moreover, their observations on the stability and the identity of the coloration of solutions of sulphammonium containing very different proportions of sulphur and ammonia, show that Moissan's conclusions regarding the existence of sulphammonium as a type of ammonium compound are not disproved.

Compounds of Silicon and Molybdenum. Molybdenum Disilicide.—Ed. Defacqz.—When a mixture of copper silicide and amorphous molybdenum (obtained by the reduction of the oxide by hydrogen at a red heat) is heated in the electric furnace, grey crystals of a silicide of molybdenum having the formula Si_2Mo are obtained. The density of the compound is 6·2 at 0°; it is non-magnetic. It is attacked by chlorine at 350—400°, giving silicon tetrachloride and molybdenum pentachloride. Aqua regia containing hydrofluoric acid dissolves it easily when heated with it on a water-bath, giving a clear liquid from which a residue of molybdic acid is obtained upon evaporation. Soda, potash, and alkaline carbonates convert it into a mixture of silicate and alkaline molybdate. Boiling hydrochloric acid, nitric acid, and sulphuric acid have no action upon it.

Different Molecular States of Anhydrous and Hydrated Ferric Sulphate.—A. Recoura.—The author has already described three varieties of ferric sulphate with very different properties, one of them anhydrous, and the others isomeric hydrates: $Fe_2O_3.3SO_3.9H_2O$ (yellow and white). When the white hydrated sulphate is kept at a temperature a little below 100° it loses six molecules of water. If the temperature is then raised to 175° the dehydration is complete, but the yellowish brown anhydrous compound differs from the ordinary anhydrous sulphate in that it dissolves in water in a few minutes. When exposed to moist air also it behaves differently, being hydrated much more rapidly, and giving neither the yellow nor the white sulphate, but a third hydrated variety, which is also obtained by keeping the white hydrated sulphate at a temperature below 100°. It differs from the other two hydrated sulphates in that it dissolves very rapidly in alcohol (in about one hour). These five hydrates are not the only ones that exist; the action of heat on the yellow hydrated sulphate yields other varieties.

Cuprous Iodide.—Marcel Guichard.—If dry hydriodic acid is passed over anhydrous cuprous chloride at the ordinary temperature, heat is evolved and some iodine is liberated. If the product of the reaction is evaporated *in vacuo* at 40°, the free iodine sublimes and a white substance, cuprous iodide, remains behind. When prepared in the wet way by the action of alkaline iodides or hydriodic acid upon cupric salts in solution, cuprous iodide, whether dried at a low temperature or at 130°, retains a small quantity of water (much less than a molecule), which it gives up only with difficulty. When heated in air, even below 200°, it oxidises, losing iodine, but *in vacuo* at about 300° dehydration is complete. When it is heated *in vacuo* it turns yellow, and fuses to a brown liquid at 600°, and on cooling passes back through the same changes of colour to a white solid. The author analysed the compound by heating it in air and weighing the copper oxide and iodine thus formed, and obtained results which agree very closely with those calculated for anhydrous cuprous iodide.

Alloys of Cobalt and Tin.—F. Ducelliez.—The author has prepared alloys of cobalt and tin by heating the two metals in a current of hydrogen in a Schlœsing furnace. The alloys obtained are very different in appearance according to the amount of tin they contain. When the amount present is above 85 per, cent they resemble tin and can be cut; below 85 per cent they are hard and brittle. If alloys containing 80 to 92 per cent of tin are treated with nitric acid and boiled, then the residue is treated with metastannic

acid, and the residue from this process treated with fused potash and washed, a grey metallic powder is obtained which has the formula CoSn. Its density is 8·95 at 0°. Chlorine and oxygen both attack it, and sulphur vapour gives fused sulphides at a red heat. Hydrochloric acid and sulphuric acid completely dissolve it, but dilute nitric acid has no effect, even when boiled; hot concentrated nitric acid and alkaline carbonates act slowly upon it, and alkaline nitrates and potassium chlorate oxidise it with difficulty.

A Molybdo-uranium Compound.—André Lancien.—When ammonium molybdate acts on uranyl nitrate a precipitate is formed which has the composition corresponding to the formula $MoO_4.UrO_2$, and is therefore a molybdate of uranyl. The yield is theoretical, and in the dark an amorphous white powder is obtained. It is insoluble in water, ethyl and methyl alcohol, acetic acid, chloroform, benzene, toluene, and sulphuric ether. Ethyl and methyl alcohol and acetic acid transform it into a green uranous compound. When boiled for a long time with the bases NH_3, KOH, NaOH it turns brick-red, and then gives a green oxide. It dissolves quickly in HCl, H_2SO_4, HNO_3, $H_2S_2O_7$. Its physical and chemical properties appear to change after it has been kept for thirty hours; it is then yellow in colour, insoluble in HNO_3, and not reduced by ethyl alcohol. It is a radio-active substance, and its activity is about equal to that of barium bromide, and much superior to that of uranyl nitrate.

Lupeol.—E. Jungfleisch and H. Leroux.—From the guttapercha of *Palaquium Treubi* the authors have isolated a cinnamic ether which is identical with the cinnamate of lupeol. In the course of their experiments they found that lupeol when heated loses water, giving a hydrocarbon, which may be called lupeylene. The analysis of lupeol, its cinnamate, and lupeylene, led to the formula $C_{30}H_{50}O$ for the alcohol, which is that of a monovalent alcohol, derived from a triterpene; the alcohol derivatives of the terpenes, the isocamphenols, when heated readily give a hydrocarbon and water, thus resembling lupeol. The fact that the action of bromine upon lupeol has led to different results in the hands of different observers is to be explained by this transformation into water and hydrocarbon.

Action of Ethereal Salts of α-Iodo Fatty Acids upon Phenylamine Magnesium Iodide and Ortho-toluidine Magnesium Iodine.—F. Bodroux and F. Taboury.—Ethyl iodo-acetate reacts normally on ortho-toluidine magnesium iodide (in solution), but has practically no action upon phenylamine magnesium iodide (precipitated). The authors thought that this difference was due to the physical states in which the organo-magnesium compound was employed, and repeated the experiment with phenylamine magnesium iodide, using enough ethyl oxide to keep the organo-metallic substance in solution. It was then found that iodo-acetanilide was formed.

$$CH_2I{-}COOC_2H_5 + 2C_6H_5{-}NH{-}Mg{-}I =$$

$$= CH_2I{-}C(=O{-}Mg{-}I)(NH{-}C_6H_5)(NH{-}C_6H_5) + Mg{<}^{I}_{OC_2H_5}.$$

$$CH_2I{-}C(=O{-}Mg{-}I)(NH{-}C_6H_5)(NH{-}C_6H_5) + 2HCl =$$

$$= Mg{<}^{I}_{Cl} + C_6H_5{-}NH_2{-}HCl + CH_2I{-}CO{-}NH{-}C_6H_5.$$

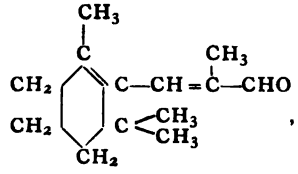
Similarly, when ethyl α-iodo-propionate and butyrate are used, the corresponding compounds, *e.g.*, $CH_3{-}CHI{-}CO{-}NH{-}C_6H_5$, &c., are obtained. These compounds are solids, crystallising in white needles, and slowly turning yellow under the influence of light.

Origin of Deposits of Colouring Matter in Red Wines.—A. Trillat.—Pasteur has shown that red wine when protected from the air can be kept indefinitely without any deposit being formed, but when the wine is exposed to the air the colouring matter is oxidised and a deposit is formed. The author has proved that the colouring matter of red wine whem dissolved in a dilute acid in absence of alcohol can be kept for a long time in contact with oxygen without undergoing any change, while the addition of aldehyde produces a precipitate. The further examination of this point shows that the conversion of the alcohol of wine into aldehyde is one of the causes, if not the principal cause, of the formation of the deposits.

Synthesis of an Aldehyde with an Odour of Violets.—Ph. Barbier.—Citral condenses with propanol, giving a mixture of two isomers with the formula $C_{13}H_{20}O$. The structural formula of the first isomer, which boils at 147—148° under 13 mm., is—

$$CH_3{-}C(CH_3){=}CH{-}CH_2{-}CH_2{-}C(CH_3){=}CH{-}CH{-}C(CH_3){-}CHO,$$

and it is thus an unsaturated aldehyde. When dissolved in sulphuric acid, heated to 50° or 60°, and cooled, two isomers of the cyclic aldehyde—



are obtained. These aldehydes have a strong odour of fresh violets. They oxidise very readily in air, and cannot therefore be used as a substitute for ionone, to which they are greatly superior in odour.

MISCELLANEOUS.

City and Guilds of London Institute.—At a meeting of the Council of the City and Guilds of London Institute held on the 22nd inst. it was resolved to confer the Fellowship of the Institute (F.C.G.I.) upon Mr. Alfred E. Young, A.C.G.I., A.M.I.C.E., F.R.A.S., F.R.G.S., Chief Surveyor of the Federated Malay States, for his original and valuable work in the Trigonometrical Survey of the Malay States. Mr. Young matriculated at the City and Guilds Central Technical College in 1877, he obtained the John Samuel Scholarship at the end of 1889, and was awarded the Diploma of "Associate" of the Institute in 1890.

Institute of Chemistry.—*Pass List of the July Examinations*, 1907.—Of twenty-eight candidates who entered for the Intermediate Examination, the following twenty-two passed: N. C. Akers, A. D. Black, J. Boyd, J. Brebner, M.A., B.Sc. (Aberdeen), R. Bruce, A. M. Cameron, B.Sc. (Edin.), H. R. Cooper, B.Sc. (Lond.), F. G. Crosse, W. C. Davis, M. C. Fletcher, H. L. Gammon, J. Gibbon, N. McN. Hyslop, R. D. Masson, R. L. Morris, J. W. H. Pattison, A. S. Petrie, O. D. Roberts, W. F. Russell, A. Sandeman, P. A. W. Self, B.Sc. (Lond.), and Miss Maggie Millen Jeffs Sutherland. In the Final Examination for the Associateship (A.I.C.), of five examined in the Branch of Mineral Chemistry, three passed: William Garsed, William Godden, Assoc.R.C.Sc. (Lond.), B.Sc. (Lond.), and Eric Hayward. Of two examined in the Branch of Metallurgical Chemistry, one passed: E. B. Naylor, M.Sc. (Manchester). Of five examined in Organic Chemistry, three passed: F. Baker, B.Sc. (Lond.), J. H. Lane, and B. D. W. Luff. Of seven (including one Associate) who entered in the Branch of the Analysis of Food and Drugs and of Water, including an Examination in Therapeutics, Pharmacology, and Microscopy, the following four passed: R. R. Bennett, F. M. Dyke, B.Sc. (Lond.), W. R. S. Ladell, and D. J. Law, B.Sc. (Lond.).

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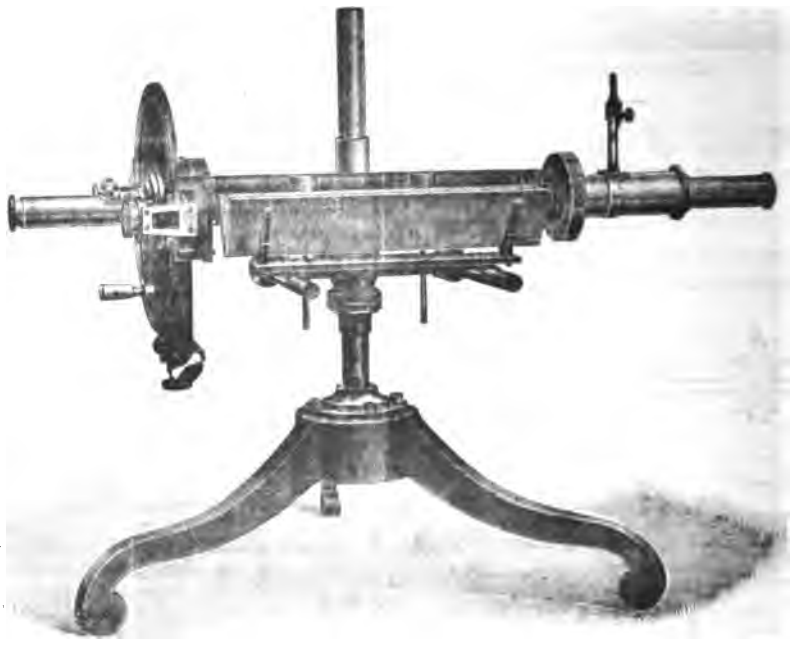

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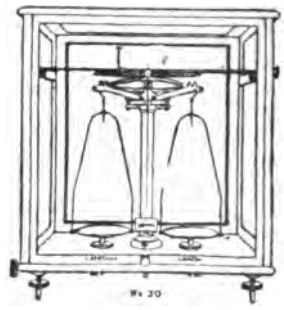

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BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

LEICESTER, 1907.

INAUGURAL ADDRESS OF THE PRESIDENT,

Sir DAVID GILL, K.C.B., LL.D., D.Sc., F.R.S., Hon. F.R.S.E., &c.

TO-NIGHT, for the first time in its history, the British Association meets in the ancient city of Leicester; and it now becomes my privilege to convey to you, Mr. Mayor, and to the citizens generally, an expression of our thanks for your kind invitation and for the hospitable reception which you have accorded to us.

Here in Leicester and last year in York, the Association has followed its usual custom of holding its annual meeting somewhere in the United Kingdom; but in 1905 the meeting was, as you know, held in South Africa. Now, having myself only recently come from the Cape, I wish to take this opportunity of saying that this southern visit of the Association has, in my opinion, been productive of much good; wider interest in science has been created amongst colonists, juster estimates of the country and its problems have been formed on the part of the visitors, and personal friendships and interchange of ideas between thinking men in South Africa and at home have arisen which cannot fail to have a beneficial influence on the social, political, and scientific relations between these colonies and the mother country. We may confidently look for like results from the proposed visit of the Association to Canada in 1909.

One is tempted to take advantage of the wide publicity given to words from this chair to speak at large in the cause of science, to insist upon the necessity for its wider inclusion in the education of our youth and the devotion of a larger measure of the public funds in aid of scientific research; to point to the supreme value of science as a means for the culture of those faculties which in man promote that knowledge which is power; and to show how dependent is the progress of a nation upon its scientific attainment.

But in recent years these truths have been prominently brought before the Association from this Chair; they have been exhaustively demonstrated by Sir William Huggins from the Chair of the Royal Society, and now a special guild (the British Science Guild) exists for their enforcement upon the mind of the nation.

These considerations appear to warrant me in following the healthy custom of so many previous Presidents, viz., of confining their remarks mainly to those departments of science with which the labours of their lives have been chiefly associated.

The Science of Measurement.

Lord Kelvin in 1871 made a statement from the Presidential Chair of the Association at Edinburgh as follows:—"Accurate and minute measurement seems to the non-scientific imagination a less lofty and dignified work than the looking for something new. But nearly all the grandest discoveries of science have been the reward of accurate measurement and patient long-continued labour in the minute sifting of numerical results."

Besides the instances quoted by Lord Kelvin in support of that statement, we have perhaps as remarkable and typical an exemplification as any in Lord Rayleigh's long-continued work on the density of nitrogen which led him to the discovery of argon. We shall see presently that, true as Lord Kelvin's words are in regard to most fields of science, they are especially applicable as a guide in astronomy.

One of Clerk Maxwell's lectures in the Natural Philosophy Class at Marischall College, Aberdeen, when I was a student under him there, in the year 1859, ran somewhat as follows:—

> A standard, as it is at present understood in England, is not a real standard at all; it is a rod of metal with lines ruled upon it to mark the yard, and it is kept somewhere in the House of Commons. If the House of Commons catches fire there may be an end of your standard. A copy of a standard can never be a real standard, because all the work of human hands is liable to error. Besides, will your so-called standard remain of a constant length? It certainly will change by temperature, it probably will change by age (that is, by the rearrangement or settling down of its component molecules), and I am not sure if it does not change according to the azimuth in which it is used. At all events, you must see that it is a very impractical standard—impractical because if, for example, any one of you went to Mars or Jupiter, and the people there asked you what was your standard of measure, you could not tell them, you could not reproduce it, and you would feel very foolish. Whereas, if you told any capable physicist in Mars or Jupiter that you used some natural invariable standard, such as the wave-length of the D line of sodium vapour, he would be able to reproduce your yard or your inch, provided that you could tell him how many of such wave-lengths there were in your yard or your inch, and your standard would be available anywhere in the universe where sodium is found.

That was the whimsical way in which Clerk Maxwell used to impress great principles upon us. We all laughed before we understood; then some of us understood and remembered.

Now the scientific world has practically adopted Maxwell's form of natural standard. It is true that it names that standard the metre; but that standard is not one-millionth of the Earth's quadrant in length, as it was intended to be; it is merely a certain piece of metal approximately of that length.

It is true that the length of that piece of metal has been reproduced with more precision, and is known with higher accuracy in terms of many secondary standards, than is the length of any other standard in the world; but it is, after all, liable to destruction and to possible secular change of length. For these reasons it cannot be scientifically described otherwise than as a piece of metal whose length at 0° C. at the epoch A.D. 1906 is = 1,553,164 times the wave-length of the red line of the spectrum of cadmium when the latter is observed in dry air at the temperature of 15° C. of the normal hydrogen-scale at a pressure of 760 mm. of mercury at 0° C.

This determination, recently made by methods based on the interference of light-waves and carried out by MM. Perot and Fabry at the International Bureau of Weights and Measures, constitutes a real advance in scientific metrology. The result appears to be reliable within one ten-millionth part of the metre.

The length of the metre, in terms of the wave-length of the red line in the spectrum of cadmium, had been determined in 1892 by Michelson's method, with a mean result in almost exact accordance with that just quoted for the comparisons of 1906; but this agreement (within one part in ten millions) is due in some degree to chance, as the uncertainty of the earlier determination was probably ten times greater than the difference between the two independent results of 1892 and 1906.

We owe to M. Guillaume, of the same International Bureau, the discovery of the remarkable properties of the

alloys of nickel and steel, and from the point of view of exact measurement the specially valuable discovery of the properties of that alloy which we now call "invar." He has developed methods for treatment of wires made from this alloy which render more permanent the arrangement of their constituent molecules. Thus these wires, with their attached scales, may, for considerable periods of time and under circumstances of careful treatment, be regarded as nearly invariable standards. With proper precautions, we have found at the Cape of Good Hope that these wires can be used for the measurement of base lines of the highest geodetic precision with all the accuracy attainable by the older and most costly forms of apparatus; whilst with the new apparatus a base of 20 kilometres can be measured in less time and far less cost than one of a single kilometre with the older forms of measurement.

The Great African Arc of Meridian.

In connection with the progress of geodesy, time only permits me to say a few words about the Great African arc on the 30th meridian, which it is a dream of my life to see completed.

The gap in the arc between the Limpopo and the previously executed triangulation in Rhodesia, which I reported to the Association at the Johannesburg meeting in 1905, has now been filled up. My own efforts, at 6000 miles distance, had failed to obtain the necessary funds, but at Sir George Darwin's instance contributions were obtained from this Association, from the Royal Society and others, to the extent of half the estimated cost; the remaining half was met by the British South Africa Company. But for Darwin's happy intervention, which enabled me to secure the services of Captain Gordon and his party before the Transvaal Survey Organisation was entirely broken up, this serious gap in the great work would probably have long remained; for it is one thing to add to an existing undertaking of the kind, it is quite another to create a new organisation for a limited piece of work.

Since then Colonel (now Sir William) Morris has brought to a conclusion the reductions of the geodetic survey of the Transvaal and Orange River Colony, and his report is now in my hands for publication.

Dr. Rubin, under my direction, at the cost of the British South Africa Company, has carried the arc of meridian northwards to S. latitude 9° 42′, so that we have now continuous triangulation from Cape L'Agulhas to within fifty miles of the southern end of Lake Tanganyika; that is to say, a continuous geodetic survey extending over twenty-five degrees of latitude.

It happens that, for the adjustment of the international boundary between the British Protectorate and the Congo Free State, a topographic survey is at the present moment being executed northward along the 30th meridian from the northern border of German East Africa. A proposal on the part of the Royal Society, the Royal Geographical Society, the British Association, and the Royal Astronomical Society has been made to strengthen this work by carrying a geodetic triangulation through it along the 30th meridian, and thus adding 2½° to the African arc. These Societies together guarantee £1000 towards the cost of the work, and ask for a like sum from Government to complete the estimated cost. The topographic survey will serve as the necessary reconnaisance. The topographic work will be completed by the end of January next, and the four following months offer the best season of the year for geodetic operations in these regions.

There is a staff of skilled officers and men on the spot sufficient to complete the work within the period mentioned, and the Intercolonial Council of the Transvaal and Orange River Colony most generously offers to lend the necessary geodetic instruments. The work will have to be done sooner or later, but if another expedition has to be organised for the purpose the work will then cost from twice to three times the present amount. One cannot therefore doubt that His Majesty's Government will take advantage of the present offer and opportunity to vote the small sum required. This done, we cannot doubt that the German Government will complete the chain along the eastern side of Lake Tanganyika, which lies entirely within their territory. Indeed, it is no secret that the Berlin Academy of Sciences has already prepared the necessary estimates with a view to recommending action on the part of its Government.

Captain Lyons, who is at the head of the survey of Egypt, assures me that preliminary operations towards carrying the arc southwards from Alexandria have been begun, and we have perfect confidence that in his energetic hands the work will be prosecuted with vigour. In any case the completion of the African arc will rest largely in his hands. That arc, if ever my dream is realised, will extend from Cape L'Agulhas to Cairo, thence round the eastern shore of the Mediterranean and the islands of Greece, and there meet the triangulation of Greece itself, the latter being already connected with Struve's great arc, which terminates at the North Cape in lat. 70° N. This will constitute an arc of 105° in length—the longest arc of meridian that is measurable on the earth's surface.

The Solar Parallax.

Much progress has been made in the exact measurement of the great fundamental unit of astronomy—the solar parallax.

Early in 1877 I ventured to predict that we should not arrive at any certainty as to the true value of the solar parallax from observations of transits of Venus, but that the modern heliometer applied to the measurement of angular distances between stars and the star-like images of minor planets would yield results of far higher precision ("The Determination of the Solar Parallax," *The Observatory*, vol. i., p. 280).

The results of the observations of the minor planets Iris, Victoria, and Sappho at their favourable oppositions in the years 1888 and 1889, which were made with the co-operation of the chief heliometer and meridian observatories, fully justified this prediction (*Annals of the Cape Observatory*, vol. vi., Part 6, p. 29). The Sun's distance is now almost certainly known within one-thousandth part of its amount. The same series of observations also yielded a very reliable determination of the mass of the Moon.

The more recently discovered planet Eros, which in 1900 approached the Earth within one-third of the mean distance of the Sun, afforded a most unexpected and welcome opportunity for re-determining the solar parallax—an opportunity which was largely taken advantage of by the principal observatories of the northern hemisphere. Unfortunately the high northern declination of the planet prevented its observation at the Cape and other southern observatories. So far as the results have been reduced and published they give an almost exact accordance with the value of the solar parallax derived from the heliometer observations of the minor planets, Iris, Victoria, and Sappho in 1888 and 1889 (see *Monthly Notices R.A.S.*, Hinks, vol. lxiv., p. 725; Christie, vol. lxvii., p. 382).

But in 1931 Eros will approach the Earth within one-sixth part of the Sun's mean distance, and the fault will rest with astronomers of that day if they do not succeed in determining the solar parallax within one ten-thousandth part of its amount.

To some of us who struggled so hard to arrive at a tenth part of this accuracy under the less favourable geometrical conditions that were available before the discovery of Eros, how enviable seems the opportunity!

And yet, if we come to think of it rightly, the true opportunity and the chief responsibility is ours, for *now* and not twenty years hence is the time to begin our preparation; *now* is the time to study the origin of those systematic errors which undoubtedly attach to some of our photographic processes; and then we ought to construct telescopes specially designed for the work. These telescopes should be applied to the charting of the stars near

the path which Eros will describe at its opposition in 1931, and the resulting star-co-ordinates derived from the plates photographed by the different telescopes should be rigorously intercompared. Then, if all the telescopes give identical results for the star-places, we can be certain that they will record without systematic error the position of Eros. If they do not give identical results, the source of the errors must be traced.

The planet will describe such a long path in the sky during the opposition of 1931 that it is already time to begin the meridian observations which are necessary to determine the places of the stars that are to be used for determining the constants of the plates. It is desirable, therefore, that some agreement should be come to with respect to selection of these reference stars, in order that all the principal meridian observatories in the world may take part in observing them.

I venture to suggest that a Congress of Astronomers should assemble in 1908 to consider what steps should be taken with reference to the important opposition of Eros in 1931.

The Stellar Universe.

And now to pass from consideration of the dimensions of our solar system to the study of the stars, or other suns, that surround us.

To the lay mind it is difficult to convey a due appreciation of the value and importance of star-catalogues of precision. As a rule such catalogues have nothing whatever to do with discovery in the ordinary sense of the word, for the existence of the stars which they contain is generally well known beforehand; and yet such catalogues are, in reality, by far the most valuable assets of astronomical research.

If it be desired to demarcate a boundary on the Earth's surface by astronomical methods, or to fix the position of any object in the heavens, it is to the accurate star catalogue that we must refer for the necessary data. In that case the stars may be said to resemble the trigonometrical points of a survey, and we are only concerned to know from accurate catalogues their positions in the heavens at the epoch of observation. But in another and grander sense the stars are not mere landmarks, for each has its own apparent motion in the heavens which may be due in part to the absolute motion of the star itself in space, or in part to the motion of the solar system by which our point of view of surrounding stars is changed.

If we desire to determine these motions and to ascertain something of the general conditions which produce them, if we would learn something of the dynamical conditions of the universe and something of the velocity and direction of our own solar system through space, it is to the accurate star catalogues of widely separated epochs that we must turn for a chief part of the requisite data.

The value of a star-catalogue of precision for present purposes of cosmic research varies as the square of its age and the square of its accuracy. We cannot alter the epoch of our observations, but we can increase their value fourfold by doubling their accuracy. Hence it is that many of our greater astronomers have devoted their lives chiefly to the accumulation of meridian observations of high precision, holding the view that to advance such precision is the most valuable service to science they could undertake, and comforted in their unselfish and laborious work only by the consciousness that they are preparing a solid foundation on which future astronomers may safely raise the superstructure of sound knowledge.

But since the extension of our knowledge of the system of the universe depends quite as much on past as on future research, it may be well, before determining upon a programme for the future, to consider briefly the record of meridian observation in the past for both hemispheres.

The Comparative State of Astronomy in the Northern and Southern Hemispheres.

It seems probable that the first express reference to southern constellations in known literature occurs in the Book of Job (ix. 9): "Which maketh Arcturus, Orion, and Pleiades, and the chambers of the south." Schiaparelli's strongly supported conjecture is that the expression "chambers of the south," taken with its context, signifies the brilliant stellar region from Canopus to α Centauri, which includes the Southern Cross and coincides with the most brilliant portion of the Milky Way.

About the year 750 B.C. (the probable date of the Book of Job) all these stars culminated at altitudes between 5° and 16° when viewed from the latitude of Judæa; but now, owing to precessional change, they can only be seen in a like striking manner from a latitude about 12° further south.

The words of Dante have unquestionably originated the wonderful net of poetic fancy that has been woven about the asterism, which we now call Crux.

> To the right hand I turned, and fixed my mind
> On the other pole attentive, where I saw
> Four stars ne'er seen before save by the ken
> Of our first parents—Heaven of their rays
> Seemed joyous. O thou northern site! bereft
> Indeed, and widowed, since of these deprived.

All the commentators agree that Dante here referred to the stars of the Southern Cross.

Had Dante any imperfect knowledge of the existence of these stars, any tradition of their visibility from European latitudes in remote centuries, so that he might poetically term them the stars of our first parents?

Ptolemy catalogues them as 31, 32, 33, and 34 Centauri, and they are clearly marked on the Borgian globe described by Assemanus in 1790. This globe was constructed by an Arabian in Egypt: it bears the date 622 Hegira, corresponding with A.D. 1225, and it is possible that Dante may have seen it.

Amerigo Vespucci, as he sailed in tropical seas, apparently recognised in what we now call Crux the four luminous stars of Dante; for in 1501 he claimed to be the first European to have looked upon the stars of our first parents. His fellow-voyager, Andrea Corsali, wrote about the same time to Giuliano di Medici describing "the marvellous cross, the most glorious of all the celestial signs."

Thus much mysticism and romance have been woven about this constellation, with the result that exaggerated notions of its brilliancy have been formed, and to most persons its first appearance, when viewed in southern latitudes, is disappointing.

To those, however, who view it at upper culmination for the first time from a latitude a little south of the Canary Islands, and who at the same time make unconsciously a mental allowance for the absorption of light to which one is accustomed in the less clear skies of Northern Europe, the sight of the upright cross, standing as if fixed to the horizon, is a most impressive one. I at least found it so on my first voyage to the Cape of Good Hope. But how much more strongly must it have appealed to the mystic and superstitious minds of the early navigators as they entered the unexplored seas of the northern tropic! To them it must have appeared the revered image of the Cross pointing the way on their southward course—a symbol and sign of Hope and Faith on their entry to the unknown.

The first general knowledge of the brighter stars of the southern hemisphere we owe to Frederick de Hautman, who commanded a fleet sent by the Dutch Government in 1595 to the Far East for the purpose of exploring Japan. Hautman was wrecked and taken prisoner at Sumatra, and whilst there he studied the language of the natives and made observations of the positions and magnitudes of the fixed stars of the southern hemisphere. (The resulting catalogue of 304 stars is printed as an appendix to Hautman's *Vocabulary of the Malay Language*, published at Amsterdam in 1603.)

Our distinguished countryman Halley visited St. Helena in 1677 for the purpose of cataloguing the stars of the southern hemisphere. He selected a station now marked

Halley's Mount on the Admiralty chart of the island. I have visited the site, and the foundations of the observatory still remain. Halley's observations were much hindered by cloud. On his return to England, Halley in 1679 published his "Catalogus Stellarum Australium," containing the magnitudes, latitudes, and longitudes of 341 stars, which, with the exception of seven, all belonged to the southern hemisphere.

But the first permanently valuable astronomical work in the southern hemisphere was done in 1751-52 by the Abbé de Lacaille. He selected the Cape of Good Hope as the scene of his labours, because it was then perhaps the only spot in the world situated in a considerable southern latitude which an unprotected astronomer could visit in safety, and where the necessary aid of trained artisans to erect his observatory could be obtained. Lacaille received a cordial welcome at the hands of the Dutch governor Tulbagh; he erected his observatory in Cape Town, made a catalogue of nearly 10,000 stars, observed the opposition of Mars, and measured a short arc of meridian all in the course of a single year. Through his labours the Cape of Good Hope became the birthplace of astronomy and geodesy in the southern hemisphere

Bradley was laying the foundations of exact astronomy in the northern hemisphere at the time when Lacaille laboured at the Cape. But Bradley had superior instruments to those of Lacaille, and much longer time at his disposal. Bradley's work is now the basis on which the fair superstructure of modern astronomy of precision rests. His labours were continued by his successors at Greenwich, and by a long series of illustrious men like Piazzi, Groombridge, Bessel, Struve, and Argelander. But in the southern hemisphere the history of astronomy is a blank for seventy years from the days of Lacaille.

We owe to the establishment of the Royal Observatory at the Cape by an Order in Council of 1820 the first successful step towards the foundation of astronomy of high precision in the southern hemisphere.

Time does not permit me to trace in detail the labours of astronomers in the southern hemisphere down to the present day; and this is the less necessary because in a recent Presidential Address to the South African Philosophical Society I have given in great part that history in considerable detail (*Trans. South African Phil. Soc.*, vol. xiv., Part 2). But I have not there made adequate reference to the labours of Dr. Gould and Dr. Thome at Cordoba. To their labours, combined with the work done under Stone at the Cape, we owe the fact that for the epoch 1875 the meridian sidereal astronomy of the southern hemisphere is nearly as well provided for as that of the northern. The point I wish to make is that the facts of exact sidereal astronomy in the southern hemisphere may be regarded as dating nearly a hundred years behind those of the northern hemisphere.

The Constitution of the Universe.

It was not until 1718, when Edmund Halley, afterwards Astronomer Royal of England, read a paper before the Royal Society, entitled "Considerations on the Change of the Latitudes of some of the Principal Fixt Stars," that any definite facts were known about the constitution of the universe (*Phil. Trans.*, 1718, p. 738). In that paper Halley, who had been investigating the precession of the equinoxes, says:—"But while I was upon this enquiry I was surprized to find the Latitudes of three of the principal Stars in heaven directly to contradict the supposed greater obliquity of the Ecliptick, which seems confirmed by the Latitudes of most of the rest."

This is the first mention in history of an observed change in the relative position of the so-called fixed stars—the first recognition of what we now call "proper motion."

Tobias Mayer, in 1760, seems to have been the first to recognise that if our Sun, like other stars, has motion in space, that motion must produce apparent motion amongst the surrounding stars; for in a paper to the Göttingen Academy of Sciences he writes:—"If the Sun, and with it the planets and the Earth which we inhabit, tended to move directly towards some point in the heavens, all the stars scattered in that region would seem to gradually move apart from each other, whilst those in the opposite quarter would mutually approach each other. In the same manner one who walks in the forest sees the trees which are before him separate, and those that he leaves behind approach each other." No statement of the matter could be more clear; but Mayer with the meagre data at his disposal, came to the conclusion that "the motions of the stars are not governed by the above or any other common law, but belong to the stars themselves."

Sir William Herschel, in 1783, made the first attempt to apply, with any measure of success, Mayer's principle to a determination of the direction and amount of the solar motion in space (*Phil. Trans.*, 1783, p. 247). He derived, as well as he could from existing data, the proper motions of fourteen stars, and arrived by estimation at the conclusion that the Sun's motion in space is nearly in the direction of the star λ Herculis, and that 80 per cent of the apparent motions of the fourteen stars in question could be assigned to this common origin.

This conclusion rests in reality upon a very slight basis, but the researches of subsequent astronomers show that it was an amazing accidental approach to truth—indeed, a closer approximation than Herschel's subsequent determinations of 1805 and 1806, which rested on wider and better data (*Phil. Trans.*, 1805, p. 233; 1806, p. 205).

Consider for a moment the conditions of the problem. If all the stars except our Sun were at rest in space, then, in accordance with Mayer's statement, just quoted, all the stars would have apparent motions on great circles of the sphere away from the apex and towards the antapex of the solar motion. That is to say, if the position of each star of which the apparent motion is known was plotted on the surface of a sphere and a line with an arrow-head drawn through each star showing the direction of its motion on the sphere, then it should be possible to find a point on the sphere such that a great circle drawn from this point through any star would coincide with the line of direction of that star's proper motion. The arrow-heads would all point to that intersection of the great circles which is the antapex of the solar motion, and the other point of intersection of the great circles would be the apex; that is to say, the direction of the Sun's motion in space.

But as the apparent stellar motions are small and only determinable with a considerable percentage of error, it would be impossible to find any point on the sphere such that every great circle passing through it and any particular star, would in every case be coincident with the observed direction of motion of that star.

Such discordances would, on our original assumption, be due to errors of observation, but in reality much larger discordances will occur, which are due to the fact that the other stars (or suns) have independent motions of their own in space. This at once creates a new difficulty, viz., that of defining an absolute locus in space. The human mind may exhaust itself in the effort, but it can never solve the problem. We can imagine, for example, the position of the Sun at any moment to be defined with reference to any number of surrounding stars, but by no effort of imagination can we devise means of defining the *absolute* position of a body in space without reference to surrounding material objects. If, therefore, the referring objects have unknown motions of their own, the rigour of the definition is lost.

What we call the observed proper motion of a star has three possible sources of origin.

1. The *parallactic motion*, or the effect of our Sun's motion through space, whereby our point of view of sur rounding celestial objects is changed.

2. The *peculiar* or particular motion of the star, *i.e.*, its own *absolute* motion in space.

3. That part of the observed or tabular motion which is due to inevitable error of observation.

In all discussions of the solar motion in space, from that

of Herschel down till a recent date, it has been assumed that the peculiar motions of the stars are arranged at random, and may therefore be considered zero in the mean of a considerable number of them. It is then possible to find such a value for the Precession, and such a common apex for the solar motion as shall leave the residual peculiar motions of the stars under discussion to be in the mean = zero. That is to say, we refer the motion of the Sun in space to the centre of gravity of all the stars considered in the discussion, and regard that centre of gravity as immovable in space.

In order to proceed rigorously, and especially to determine the amount as well as the direction of the Sun's motion in space, we ought to know the parallax of every star employed in the discussion, as well as its proper motion. In the absence of such data it has been usual to start from some such assumption as the following :—The stars of a particular magnitude are roughly at the same distance; those of different classes of magnitude may be derived from the hypothesis that on the average they have all equal absolute luminosity.

The assumption is not a legitimate one—

1. Because of the extreme difference in the absolute luminosity of stars.

2. Because it implies that the average absolute luminosity of stars is the same in all regions of space.

The investigation has been carried out by many successive astronomers on these lines with fairly accordant results as to the position of the solar apex, but with very unsatisfactory results as to the distances of the fixed stars (see Note). In order to judge how far the magnitude (or brightness) of a star is an index of its probable distance, we must have evidence from direct determinations of stellar parallax.

(NOTE.—Argelander, "Mém. présentés à l'Acad. Imp. des Sciences St. Pétersbourg," tome iii.; Lundahl, *Astron. Nachrichten*, No. 398, 209; Argelander, *Astron. Nachrichten*, No. 398, 210; Otto Struve, *Mém. Acad. des Sciences St. Pétersbourg*, Series 6, Math. et Phys., tome iii., p. 17: Galloway, *Phil. Trans.*, 1847, p. 79; Mädler, *Dorpat Observations*, vol. xiv., and *Ast. Nach.*, No. 566, 213; Airy, *Mem. R.A.S.*, vol. xxviii., p. 143; Dunkin, *Mem. R.A.S.*, vol. xxxii., p. 19; Stone, *Monthly Notices R.A.S.*, vol. xxiv., p. 36; De Ball, Inaugural Dissertation, Bonn, 1877; Rancken, *Astron. Nachrichten*, No. 2482, 149; Bischoff, Inaugural Dissertation, Bonn, 1884; Ludwig Struve, *Mém. Acad. St. Pétersbourg*, Series 7, tome xxxv., No. 3).

Stellar Parallax.

To extend exact measurement from our own solar system to that of other suns and other systems may be regarded as the supreme achievement of practical astronomy. So great are the difficulties of the problem, so minute the angles involved, that it is but in comparatively recent years that any approximate estimate could be formed of the true parallax of any fixed star. Bradley felt sure that if the star γ Draconis had a parallax of 1″ he would have detected it. Henderson by "the minute sifting of the numerical results" of his own meridian observations of α Centauri, made at the Cape of Good Hope in 1832-33, first obtained certain evidence of the measurable parallax of any fixed star. He was favoured in this discovery by the fact that the object he selected happened to be, so far as we yet know, the nearest sun to our own. Shortly afterwards Struve obtained evidence of a measurable parallax for α Lyræ and Bessel for 61 Cygni. Astronomers hailed with delight this bursting of the constraints which our imperfect means imposed on research. But for the great purposes of cosmical astronomy what we are chiefly concerned to know is not what is the parallax of this or that particular star, but rather what is the average parallax of a star having a particular magnitude and proper motion. The prospect of even an ultimate approximate attainment of this knowledge seemed remote. The star α Lyræ is one of the brightest in the heavens; the star 61 Cygni one that had the largest proper motion known at the time; whilst α_2 Centauri is not only a very bright star, but it has also a large proper motion. The parallaxes of these stars must therefore in all probability be large compared with the parallax of the average star; but yet to determine them with approximate accuracy long series of observations by the greatest astronomers and with the finest instruments of the day seemed necessary.

Subsequently various astronomers investigated the parallaxes of other stars having large proper motions, but it was only in 1881, at the Cape of Good Hope, that general research on stellar parallax was instituted (*Mem. R.A.S.*, vol. xlviii.). Subsequently, at Yale and at the Cape of Good Hope the work was continued on cosmical lines with larger and improved heliometers (*Annals of the Cape Observatory*, vol. viii., Part 2; and *Trans. Astron. Observatory of Yale University*, vol. i.). By the introduction of the reversing prism and by other practical refinements the possibilities of systematic error were eliminated, and the accidental errors of observation reduced within very small limits.

These researches brought to light the immense diversity in the absolute luminosity and velocity of motion of different stars. Take the following by way of example :—

Our nearest neighbour amongst the stars, α_2 Centauri, has a parallax of 0·76″, or is distant about 4½ light-years. Its mass is independently known to be almost exactly equal to that of our Sun; and its spectrum being also identical with that of our Sun, we may reasonably assume that it appears to us of the same magnitude as would our Sun if removed to the distance of α_2 Centauri.

But the average star of the same apparent magnitude as α_2 Centauri was found to have a parallax of only 0·10″, so that either α_2 Centauri or our Sun, if removed to a distance equal to that of the average fixed star of the first magnitude, would appear to us but little brighter than a star of the fifth magnitude.

Again, there is a star of only 8½ magnitude (Gould's Zones, Vh 243), which has the remarkable annual proper motion of nearly 8½ seconds of arc—one of those so-called runaway stars—which moves with a velocity of 80 miles per second at right angles to the line of sight (we no not know with what velocity in the line of sight). It is at about the same distance from us as Sirius, but it emits but one ten-thousandth part of the light energy of that brilliant star. Sirius itself emits about thirty times the light-energy of our Sun, but it in turn sinks into insignificance when compared with the giant Canopus, which emits at least 10,000 times the light-energy of our Sun.

Truly "one star differs from another star in glory." Proper motion rather than apparent brightness is the truer indication of a star's probable proximity to the Sun. Every star of considerable proper motion yet examined has proved to have a measurable parallax.

This fact at once suggests the idea, Why should not the apparent parallactic motions of the stars, as produced by the Sun's motion in space, be utilised as a means of determining stellar parallax?

Secular Parallactic Motion of Stars.

The strength of such determinations, unlike those made by the method of annual parallax, would grow with time. It is true that the process cannot be applied to the determination of the parallax of individual stars, because the peculiar motion of a particular star cannot be separated from that part of its apparent motion which is due to parallactic displacement. But what we specially want is not to ascertain the parallax of the individual star, but the mean parallax of a particular group or class of stars, and for this research the method is specially applicable, provided we may assume that the peculiar motions are distributed at random, so that they have no systematic tendency in any direction; in other words, that the centre of gravity of any extensive group of stars will remain fixed in space.

This assumption is, of course, but a working hypothesis,

and one which from the paper on star-streaming communicated by Professor Kapteyn, of Groningen, to the Johannesburg meeting of the Association two years ago we already know to be inexact (*Rep. Brit. Assoc.*, 1905, p. 257). Kapteyn's results were quite recently confirmed in a remarkable way by Eddington, using independent material discussed by a new and elegant method (*Monthly Notices R.A.S.*, vol. lxvii., p. 34). Both results showed that, at least for extensive parts of space, there are a nearly equal number of stars moving in exactly opposite directions. The assumption, then, that the mean of the peculiar motions is zero may, at least for these parts of space, be still regarded as a good working hypothesis.

Adopting an approximate position of the apex of the solar motion, Kapteyn resolved the observed proper motions of the Bradley stars into two components, viz., one in the plane of the great circle passing through the star and the apex, the other at right angles to that plane ("Publications Astron. Laboratory Groningen," Nos. 7 and 9). The former component obviously includes the whole of the parallactic motion; the latter is independent of it, and is due entirely to the real motions of the stars themselves. From the former the mean parallactic motion of the group is derived, and from the combination of the two components, the relation of velocity of the Sun's motion to that of the mean velocity of the stars of the group.

As the distance of any group of stars found by the parallactic motion is expressed as a unit in terms of the Sun's yearly motion through space, the velocity of this motion is one of the fundamental quantities to be determined. If the mean parallax of any sufficiently extensive group or class of stars was known we should have at once means for a direct determination of the velocity of the Sun's motion in space; or if, on the other hand, we can by independent methods determine the Sun's velocity, then the mean parallax of any group of stars can be determined.

Determination of Stellar Motion in the Line of Sight.

Science owes to Sir William Huggins the application of Doppler's principle to the determination of the velocity of star-motion in the line of sight. The method is now so well known, and such an admirable account of its theory and practical development was given by its distinguished inventor from this Chair at the Cardiff meeting in 1891, that further mention of that part of the matter seems unnecessary.

The Velocity of the Sun's Motion in Space.

If by this method the velocities in the line of sight of a sufficient number of stars situated near the apex and antapex of the solar motion could be determined, so that in the mean it could be assumed that their peculiar motions would disappear, we have at once a direct determination of the required velocity of the Sun's motion.

The material for this determination is gradually accumulating, and indeed much of it, already accumulated, is not yet published. But even with the comparatively scant material available, it now seems almost certain that the true value of the Sun's velocity lies between 18 and 20 kilometres per second (Kapteyn, *Ast. Nach.*, No. 3487, p. 108; and Campbell, *Astrophys. Journ.*, xiii., p. 80); or, if we adopt the mean value, 19 kilometres per second, this would correspond almost exactly with a yearly motion of the Sun through space equal to four times the distance of the Sun from the Earth.

Thus the Sun's yearly motion being four times the Sun's distance, the parallactic motion of stars in which this motion is unforeshortened must be four times their parallax. How this number varies with the amount of foreshortening is of course readily calculated. The point is that from the mean parallactic motion of a group of stars we are now enabled to derive at once its mean parallax.

This research has been carried out by Kapteyn for stars of different magnitudes. It leads to the result that the parallax of stars differing *five* magnitudes does *not* differ in the proportion of one to ten, as would follow from the supposition of equal luminosity of stars throughout the universe, but only in the proportion of about one to five (*Astron. Nachrichten*, No. 3487, Table III.; and *Ast. Journ.*, p. 566).

The same method cannot be applied to groups of stars of different proper motions, and it is only by a somewhat indirect proof, and by calling in the aid of such reliable results of direct parallax determination as we possess, that the variation of parallax with proper motion could be satisfactorily dealt with.

The Mean Parallaxes of Stars of Different Magnitude and Proper Motion.

As a final result Kapteyn derived an empirical formula giving the average parallax for stars of different spectral types, and of any given magnitude and proper motion. This formula was published at Groningen in 1901 ("Publications Astron. Laboratory Groningen, No. 88, p. 24). Within the past few months the results of researches on stellar parallax, made under the direction of Dr. Elkin, at the Astronomical Observatory of Yale University, during the past thirteen years, have been published (*Trans. Astron. Observatory of Yale University*, vol. ii. Part I.), and they afford a most crucial and entirely independent check on the soundness of Kapteyn's conclusions.

In considering the comparison between the more or less theoretical results of Kapteyn and the practical determinations of Yale, we have to remember that Kapteyn's tables refer only to the means of groups of a large number of stars having on the average a specified magnitude and proper motion, whilst the latter are direct determinations affected by the accidental errors of the separate determinations and by such uncertainty as attaches to the unknown parallaxes of the comparison stars—parallaxes which we have supplied from Kapteyn's general tables.

The Yale results consist of the determination of the parallax of 173 stars, of which only ten had been previously known to Kapteyn, and had been utilised by him. Dividing these results into groups we get the following comparison:—

Comparison Groups arranged in order of Proper Motion.

No. of stars.	Proper motion.	Magnitude.	Parallax. Yale.	Parallax. Kapteyn.	Yale—Kapteyn.
	"		"	"	"
21	0·14	3·8	0·028	0·026	+0·002
39	0·49	6·3	0·042	0·055	−0·013
45	0·59	6·7	0·068	0·060	+0·008
46	0·77	6·5	0·047	0·074	−0·027
22	1·50	6·2	0·118	0·124	−0·006
		Groups arranged in order of Magnitude.			
10	0·61	0·8	0·103	0·110	−0·007
29	0·53	3·8	0·076	0·075	+0·001
33	0·63	5·6	0·064	0·070	−0·006
34	0·73	6·7	0·055	0·070	−0·017
31	0·68	7·6	0·025	0·061	−0·036
36	0·80	8·3	0·056	0·062	−0·006
		Spectral Type I.			
13	0·42	4·0	0·076	0·076	0·000
		Spectral Type II.			
81	0·67	5·3	0·067	0·074	−0·007

These results agree in a surprisingly satisfactory way, having regard to the comparatively small number of stars in each group and the great range of parallax which we know to exist amongst individual stars having the same magnitude and proper motion. In the mean perhaps the tabular parallaxes are in a minute degree too large, but we have unquestionable proof from this comparison that our knowledge of stellar distances now rests on a solid foundation.

The Distribution of Varieties of Luminosity of Stars.

But, besides the mean parallax of stars of a particular magnitude and proper motion, it is essential that we should know approximately what percentage of the stars of such a group have twice, three times, &c., the mean parallax of

the group, and what percentage only one-half, one-third of that parallax, and so on. In principle, at least, this frequency-law may be obtained by means of the directly determined parallaxes. For the stars of which we have reliable determinations we can compare these true parallaxes with the *mean* parallax of stars having corresponding magnitude and proper motion, and this comparison will lead to a knowledge of the frequency-law required. It is true that, owing to the scarcity of material at present available, the determination of the frequency-law is not so strong as may be desirable, but further improvement is simply a question of time and the augmentation of parallax-determination.

Adopting provisionally the frequency-law found in this way by Kapteyn, we can localise all the stars in space down to about the ninth magnitude (*Publications Astron. Lab. Groningen*, No. 8, p. 23).

Take, for example, the stars of magnitude 5·5 to 6·5. There are about 4800 of these stars in the whole sky. According to Auwers-Bradley, about 9½ per cent of these stars, or some 460 in all, have proper motions between 0·04″ and 0·05.″ Now, according to Kapteyn's empiric formula, whose satisfactory agreement with the Yale results has just been shown, the mean parallax of such stars is almost exactly 0·01.″ Further, according to his frequency-law, 29 per cent of the stars have parallaxes between the *mean* value and double the mean value; 6 per cent have parallaxes between twice and three times the mean value; 1½ per cent between three and four times the mean value. Therefore of our 460 stars 133 will have parallaxes between 0·01″ and 0·02″, twenty-eight between 0·02″ and 0·03″, seven between 0·03″ and 0·04″, and so on.

Localising in the same way the stars of the sixth magnitude having other proper motions. and then treating the stars of the first magnitude, second magnitude, third magnitude, and so on to the ninth magnitude in the same way, we finally locate all these stars in space (*Ibid.*, No. 11, Table II.).

It is true we have not localised the individual stars, but we know approximately and within certain limits of magnitude the number of stars at each distance from the Sun.

Thus the apparent brightness and the distance being known we have the means of determining the light-energy or absolute *luminosity* of the stars, *provided it can be assumed that light does not suffer any extinction in its passage through interstellar space.*

On this assumption Kapteyn was led to the following results, viz., that within a sphere the radius of which is 560 light-years (a distance which corresponds with that of the average star of the ninth magnitude) there will be found :—

1 star	giving from	100,000	to	10,000	
26 stars	,,	10,000	,,	1,000	
1,300 ,,	,,	1,000	,,	100	Times the
22,000 ,,	,,	100	,,	10	light of
140,000 ,,	,,	10	,,	1	our Sun.
430,000 ,,	,,	1	,,	0·1	
650,000 ,,	,,	0·1	,,	0·01	

(To be continued).

Dichloro-chromic Bromide and Dibromo-chromic Chloride.—Neils Bjerrum.—When green chromic bromide is dissolved in dilute hydrochloric acid and precipitated with hydrochloric acid gas, meanwhile cooling with cold water, a salt is obtained, which may be filtered off when the liquid is saturated with hydrochloric acid. Analysis shows that this salt has the formula $CrBr_2Cl.6H_2O$ or $[Cr(H_2O)_4Br_2]Cl.2H_2O$. The dichloro-chromic bromide is obtained by dissolving dichloro-chromic chloride in water and adding hydrobromic acid. It is a green deliquescent crystalline powder, with the formula $[Cr(H_2O)_4Cl_2]Br$. A tetrahydrate of dibromo-chromic bromide may be prepared from chromic acid and hydrobromic acid.—*Berichte*, xl., No. 19.

EXAMINATION OF RUBBER TYRES.

By CLAYTON BEADLE and HENRY P. STEVENS.

WE have devoted a considerable amount of time and attention to the analysis and valuation of tyre rubbers, and think the results of our tests and observations will prove of general interest, as well as of practical utility. Of previous work, an interesting paper was published by the late C. O. Weber in the *Indiarubber Journal* dealing with the methods of analysis and significance of results obtained with bicycle tyres. A paper also appeared, by Schidrowitz and Kaye, in the *Journal of the Society of Chemical Industry*, Feb. 28th, 1907, giving the results of analyses obtained with a number of motor tyres; the analyses are given in detail. The results we shall here describe have been obtained with solid tyres, as the problems involved are, perhaps, simpler than with the outer cover of pneumatic tyres, where the tread is often composed of a different class of rubber to the remainder. We think, however, that most of what follows will also apply to outer covers, especially to that portion forming the tread.

The constituent of the tyre first calling for attention is the rubber itself. Although the quality of a tyre is by no means wholly dependent on the percentage of actual rubber substance or caoutchouc it contains, yet this percentage is of considerable importance in judging the value of a tyre. A satisfactory tyre cannot be made without a certain minimum percentage of rubber, although an experienced maker may succeed in producing an article of the same quality as his rival while using a smaller proportion of rubber. Any mixing, whatever the proportion of rubber, may be spoilt by errors in the manufacturing processes.

When interpreting the figure for the percentage of rubber found in the analysis of a tyre two other circumstances must be taken into consideration. The first of these is the kind of rubber used. Here we are working very much in the dark; there are data such as the percentage of resin from which some information may be gleaned, but it is difficult to draw trustworthy conclusions. The other point arises from the increasing use of recovered rubber in rubber mixings. Recovered rubber is of less value than new rubber, but analytical methods do not allow of a distinction being drawn except indirectly by the figure for vulcanisation coefficient. This latter represents the percentage of sulphur in actual chemical combination with the rubber or caoutchouc. As the methods employed in recovering waste rubber do not actually devulcanise, that is, remove combined sulphur, and as the recovered rubber when vulcanised probably combines with a further proportion of sulphur, it follows that tyre rubbers containing much recovered rubber have usually exceptionally high vulcanisation coefficients. Unfortunately, the determination of the latter involves three or four separate sulphur determinations, so that it is confined to careful and exhaustive analyses.

However, in spite of these limitations the figure for the percentage of rubber is of considerable value. It cannot be determined directly, but is obtained by difference after determining the acetone extract (chiefly resins and free sulphur), loss on boiling with alcoholic potash (rubber substitutes), and mineral matter. The latter is, of course, obtained by burning the rubber to ash.

The next figure to be considered is the percentage of matter extracted with acetone (acetone extract). This contains all free sulphur and resins. The free sulphur should not be too high, especially in the case of motor tyres which get very hot from friction. A high percentage of resin points to the use of inferior quality of rubber in the manufacture. Although the percentage of resin in a crude rubber is not proportional to the value of the rubber, nevertheless the better class of South American rubbers contain less resin in the washed and dried state than most African brands, and para contains less resin than any other variety. Indiarubber substitutes are undesirable in any class of tyre. The amount present may be judged by the loss

sustained on boiling the sample with alcoholic potash. The tensile strength is of great importance in judging the value of a tyre; as a general rule, the higher the tensile strength the better the tyre, provided that this result is attained with due regard to elasticity and distensibility. On the other hand, with certain classes of tyres, such as solid tyres, the distensibility should not be too great, otherwise the tyre is not sufficiently rigid. In the case of motor tyres which get very hot in use, the heat test should be applied. The samples are heated to a certain temperature for a definite period, and afterwards examined to see if, and to what extent, the rubber has deteriorated. The tensile strength may also be taken while the sample is hot; in this way the test is carried out under conditions which more closely resemble those to which the rubber is exposed in actual practice.

Finally, the tendency to sun cracking may be gauged by special chemical tests. This and others are described more fully at the end of this paper.

To demonstrate the aid afforded by the chemical and physical tests we have described, in forming an opinion of the value of a tyre and how it is likely to behave in use, we have chosen for illustration the results obtained in the examination of four samples, the relative merits of which we desired to ascertain.

Sample.	1.	2.	3.	4.
Resins, &c. (acetone extract), per cent.	9·0	8·6	7·2	7·4
Indiarubber substitutes (alcoholic potash extract), per cent	10·2	8·9	9·1	11·7
Mineral matter (ash), per cent	38·5	39·2	40·7	33·2
Indiarubber (caoutchouc) by difference, per cent	42·3	43·3	43·0	47·7
Total sulphur (calculated on caoutchouc), per cent ..	7·8	9·0	10·0	11·3
Free sulphur (calculated on caoutchouc), per cent ..	3·5	3·7	5·6	6·1
Combined sulphur (calculated on caoutchouc), per cent ..	4·3	5·3	4·4	5·2
Tensile strength, grms.	3718	2509	3403	3217
Elongation at rupture, per cent)	55	38·5	52	45·5
Elongation under a strain of 1500 grms., per cent	23·5	24	24·5	26·5

In addition to the above figures it should be stated that the dry heat test did not bring out any striking differences between the four samples, although Samples 1 and 2 showed up as somewhat inferior to 3 and 4. The absorption of oxygen in the sun-cracking tests was practically the same in all four samples, and was not excessive.

We will now consider these results. To begin with, the figures obtained in the analysis of Sample 4 differ from Samples 1 to 3 in the small proportion of mineral matter and corresponding high percentage of caoutchouc. This at first sight seems to point to the surperiority of Sample 4 were it not that the vulcanisation coefficient (combined sulphur) is high, which points to the possibility that part of the caoutchouc is in reality recovered rubber. The extract with alcoholic potash is also higher than in the other samples, which is, of course, to its disadvantage. There is little to choose in this respect between Samples 2 and 3, while Sample 1 contains rather more. The acetone extracts of all four samples show about the same figure; Sample 1 is rather inferior in this respect. The percentage of free sulphur, provided that it is within certain limits, is not a matter of great importance in a solid tyre; this figure is highest in the case of Sample 4. The percentage of combined sulphur is, on the other hand, of great importance, the high figures in Samples 2 and 4 point to over-vulcanisation or the presence of substitutes, and mark these two samples as inferior to the others. These conclusions are borne out by the physical tests. The tensile strengths of Samples 2 and 4 are lower than the others; this applies especially to Sample 2, which is also wanting in distensibility, showing a smaller elongation at rupture than the other samples. The figures for tensile strength and elongation of Sample 4 are particularly instructive. Containing, as it apparently does, a larger percentage of caoutchouc and a smaller percentage of mineral matter, we should have expected it to show a higher tensile strength and elongation than Samples 1 and 3, which, for reasons referred to, is not necessarily the case. We have little hesitation in ranking Samples 2 and 4 as inferior to 1 and 3, and considering the very low tensile strength of Sample 2, we should think, on the whole, that it would be inferior to Sample 4. We now have to decide which of Samples 1 and 3 is the better. In tensile strength No. 1 has the advantage, but the acetone and alcoholic potash extracts are higher, which means that in this respect No. 1 is inferior. No. 1 did not behave so well as No. 3 in the heat test. The small elongation under a medium strain must be taken in favour of No. 1. Taking all matters into consideration, we should give the preference to Sample 3. After the above analyses had been made and these conclusions drawn, the four samples were submitted to a rubber manufacturer, who, without a knowledge of our analytical figures, informed us, after an examination of the samples, the relative prices at which each could be produced. He stated that Sample 3 would be the most expensive to produce, Sample 1 coming next, while the samples of Samples 2 and 4 would be the cheapest to produce. It will therefore be seen that the conclusions drawn from our test were confirmed from a purely practical standpoint. We also learnt from an independent source that Sample 3 is one of the most satisfactory tyres on the market.

It would therefore appear that a thorough chemical and physical examination of a tyre will lead to a reliable estimation of its value.

In conclusion, we give a short description of the analytical methods.

As a result of our experience in analyses of tyre rubbers we have adopted the following methods for ordinary commercial purposes. The methods are based on the work of well-known authorities, as Henriques and Weber.

Portions are cut from the tyre and reduced to powder by passing through a mincing machine, and sufficient of the sample placed in a stoppered bottle for analysis. The mineral matter is determined by burning 1 grm. spread in an even layer on the bottom of a large porcelain crucible or small shallow dish; platinum crucibles cannot be used owing to the presence of zinc and other metals in the ash. Rubber is one of the most difficult substances to ash. It must be heated first with quite a small flame, and the rubber must not allowed to catch fire. The heating is continued, increasing the flame until the whole of the organic matter is burnt off. It should be allowed to cool in a desiccator, and weighed as soon as cold. In all cases it should be re-heated and weighed again.

The percentage of ash may be a little higher or lower than that of the mineral in the original mixing, as the mineral may contain some volatile constituents, *e.g.*, carbonic acid in the form of carbonate, and, on the other hand, some of the sulphur from the rubber may be retained by the metals as sulphides in the place of oxides, thus raising the weight of the ash. Nevertheless, the percentage of ash is a fairly accurate measure of the amount of mineral in the original mixing.

The specific gravity determination has lost much of its value as a means of detecting adulteration, owing to the use of rubber substitutes and recovered rubber. Further, it is obvious that the specific gravity of the added mineral will also produce its effect. Nevertheless, the figures for the specific gravity often bear a relation to those for ash. Take the following four samples from different sources which we recently had occasion to analyse for purposes of comparison:—

No. of sample.	Per cent ash.	Specific gravity.
1.	38·6	1·45
2.	40·9	1·51
3.	42·2	1·56
4.	42·4	1·59

We next proceed to a systematic examination to determine resin, free sulphur, and rubber substitutes. For this purpose 2 grms. of the finely powdered sample are thoroughly extracted for several hours in a Soxhlet with acetone. It is advisable to keep the extraction going for eight to ten hours. The acetone is distilled off, and the flask containing the resin and free sulphur dried in a water-oven and weighed. The contents are then exhausted four times with acetone, 2 cc. at a time, to dissolve out the resin, as suggested by Weber, and the sulphur remaining in the flask determined by drying down and weighing. A trace of sulphur dissolved by the acetone may be allowed for, but, according to Weber this only amounts to 6 mgrms. The sulphur subtracted from the total extract gives the resin. The extracted rubber is placed in a small weighing bottle, and dried in a current of coal-gas by taking out the stopper and inserting in its place a cork with inlet and outlet tubes; the coal-gas passing through is burnt underneath the water-oven in which the bottle is placed. The bottle is removed from time to time, the stopper inserted, and weighed when cold. The weight of the extracted rubber subtracted from that of the original rubber gives a rather higher figure for loss on extraction than that obtained by weighing the acetone extract. This is due to moisture in the original rubber.

The extracted rubber is introduced into a flask with inverted condenser, and boiled with weak alcoholic potash for four hours. It is then thrown on to a filter-paper and washed with hot water till no longer alkaline. The contents are transferred to the weighing-bottle, dried in a current of coal-gas as before, and weighed. The loss in weight may be taken as substitutes.

The residue will consist of rubber and mineral matter. It may be burnt to ash, and the rubber determined by difference.

We are now able to form a general opinion of the composition of the tyre. Of course it is possible to carry the analysis much further, chiefly with a view to determining the percentage of sulphur combined with the rubber or "vulcanisation coefficient." This figure is of value, but unfortunately its determination entails a good deal of analytical work.

Valuable as are the results of chemical analysis, there are certain physical tests which are of equal importance, in particular the determination of tensile strength and elongation at rupture. The most convenient method to adopt is to cut rings from sections of the tyre in thin sheets about 1 mm. thick. Discs are first cut, and the thickness of each disc is measured before puncturing. The ring is stretched between smooth iron hooks in a testing machine, and subjected to increasing tension until the ring ruptures. The tension required to rupture the ring and the elongation at the moment of rupture are noted.

The sun-cracking test is carried out by exposing thin sections of the tyres under examination to the action of a mixture of 20 grms. acetone and 60 cc. hydrogen peroxide solution (Weber). The test is a comparative one, so that the sections of tyres must be cut so as to expose the same area to the action of the mixed solutions. The pieces are weighed before immersion, and after twenty-four hours are removed, washed with a little acetone, dried, and weighed again. The increase in weight gives the amount of oxygen absorbed by the rubber, and may be taken as an indication of the tendency of the tyre to oxidise, which is the cause of "sun-cracking."

The "dry heat" test is carried out by exposing sections cut from the tyres to a temperature of 320° F. for four hours. For this purpose an ordinary hot-air oven provided with thermometer is required, and the temperature must be carefully regulated.

PRESENTATION OF ADDRESSES TO PROFESSOR LUNGE.

THE students of the Zurich Polytechnic—and especially those of the Chemical Department, to whom the retirement of Prof. Lunge is so great a loss—did not allow his final lecture to pass by without offering him some tokens of their gratitude and affection. The Professor had expressed the wish that no elaborate ceremony should be arranged, but the informal gathering gave an impressive indication of the depth of the students' feelings. The vestibule and auditorium of the Chemical Department were decorated with laurel and other leaves, in preparation for the last lecture, and the whole building was closely packed with the students, colleagues, and friends of the Professor.

When Prof. Lunge entered the auditorium, greeted by the sounds of an Adagio played by the Students' Quartette, Prof. Treadwell rose and announced that he had been deputed by the teachers of the Institution to address a few words to him. He alluded to the length of Dr. Lunge's connection with the Polytechnic, and to the great value of the work he had done for it, to his unwearied efforts on behalf of the students, his phenomenal power of work and keen sense of duty, and to the esteem and gratitude which his colleagues felt for him. In conclusion, Prof. Treadwell expressed the hope that after a thorough rest for mind and body, he might feel sufficiently refreshed to take up again the life-work to which he had devoted all his strength and energy—the advancement of science—and that he might be spared for many years of activity. At the conclusion of his speech he read the text of an Address which the whole teaching staff of the Polytechnic presented to the retiring Professor.

Herr cand. chem. Walter Eglin then offered in heartfelt terms the thanks of the students, who honoured Prof. Lunge, not only as an inimitable teacher and a skilled experimenter, but also as a noble man whose example and counsel were invaluable to them when they embarked upon their varied careers. An Address from the students was then presented to Prof. Lunge, who rose to express his thanks. Almost overcome by emotion, he explained how impossible it was for him to put into words the deep feelings which had been aroused by this ceremony, and by the severance of his official connection with the Institution, upon the staff of which were some of his oldest and most valued friends. He said that ever since, acting on the advice of his physician, he had decided to vacate his post, he had hardly had a peaceful moment, for he could not conceive what it would mean to him to renounce an occupation which had hitherto absorbed all his time and energies. The farewell of his students had now, if possible, made his heart still heavier; the trouble they had taken to decorate the building, the closely-packed assembly in the hall, the kind words—far above his deserts—which Prof. Treadwell and Herr Eglin had spoken, all this recognition of his efforts he could only regard as implying that they took the will that he had to serve them for his imperfect deeds, and he felt that the memory of this leave-taking would be a consolation to him for the rest of his life, helping him through many dark hours.

Upon the conclusion of the speech, the whole audience rose and gave expression to their feelings in hearty applause, which Prof. Lunge repeatedly acknowledged. Thus ended the little ceremony, which in its simplicity and spontaneity testified admirably to the genuine warmth of the students' feelings and the affection of his colleagues.

Society of Arts.—The Council are prepared to offer, under the terms of the Stock Trust, a Gold Medal, or a Prize of £20, for the Decoration of Part of the Interior of a Building.

NOTICES OF BOOKS.

Les Nouveautés Chimiques pour 1907. ("Chemical Novelties for 1907.") By CAMILLE POULENC. Paris: J. B. Baillière et Fils. 1907.

THIS descriptive list of all the more important modifications and improvements of apparatus which have come into use during the year 1906, like its predecessors, will be a useful guide for equipping a physical or chemical laboratory with the most modern appliances. The author appears to have overlooked no important improvement in old, or invention of new apparatus, and has selected his material carefully and judiciously. Some allusion is made to the results of recent researches, and the section on chemical analysis is particularly full. Thus the analysis of milk by Bordas and Touplan's method is discussed at length, these chemists having found that the usual methods of estimating its constituents either leave something to be desired in the way of accuracy, or else are too slow to be employed when a great number of samples have to be examined. The method they propose has the advantage of allowing a series of six samples to be analysed fully in less than three hours, and the casein is determined directly and not by difference.

CORRESPONDENCE.

RELATION BETWEEN VALENCY AND ENERGY.

To the Editor of the Chemical News.

SIR,—In the CHEMICAL NEWS (xcv., 301) Mr. Redgrove criticises an hypothesis of mine which appeared in the *Proc. Chem. Soc.*, xxiii., 134, as a preliminary note. I would therefore ask you to kindly insert the following reply:—

It is stated in the CHEMICAL NEWS, xcv., 193, that C is the heat of combustion of C in the hydrocarbons without the links, and H that of H with the C—H link. The latter is assumed to be different from the C.C link, which possesses a value L_1. It is stated that :C: in CH_4 is different from its value in C_2H_6 or in C_6H_{12}.

One of Mr. Redgrove's constants (·) is $2H - L_1 = 52{\cdot}7$, and it may also be shown that $C + 2L_1 = 105{\cdot}4$. If it be supposed that the amount added to the value of hydrogen is L, and also that $L = L_1$, the above constants may be stated as follows:—$H + \frac{L_1}{2} = H. = 26{\cdot}35$, $C + 4\frac{L_1}{2} = :C: = 105{\cdot}4$. These values are those of the isolated atoms on the above hypothesis.

It may, however, be shown by direct calculation that the numbers in question are those of the apparent atomic heats of combustion of H and C:—$2H = M.H.C.CH_4 - [CH_2] = 210{\cdot}8 - 158{\cdot}2 = 52{\cdot}6$, $H = 26{\cdot}3$; also $2H = M.H.C.\ C_2H_6 - 2[CH_2] = 52{\cdot}6$, $H = 26{\cdot}3$, $C = 158{\cdot}2 - 52{\cdot}6 = 105{\cdot}6 = 4 \times 26{\cdot}4$.

These results clearly show that $L = L_1$ whatever these may be, and, further, that they are both equal to zero, for it is evident, from the additive relations, that the numbers 26·3 and 105·6 represent either the values of the isolated atoms or that the heats concerned in the breaking and making of an equal number of links in such an equation as $C{\equiv}H_4 + 2O = O = C{\leqq}^{O}_{O} + 2^{H}_{H}{>}O$ exactly compensate one another.

The values L and L_1 have thus no significance when used in the above connection, and may therefore be neglected.

If the links be taken into account (on the latter assumption), it follows that :C: : H. = X : Y, numbers $> 105{\cdot}6$ and $> 26{\cdot}3$ respectively; that is, $>$ the apparent atomic heats of combustion of C and H.

If the unknown values :C: and H., however, be considered, it follows from the fact that $:C: = C + 4\frac{L_1}{2} = X$ and $H. = H + \frac{L_1}{2} = Y$ that the values of the isolated atoms are still in the ratio of 4 : 1, which is similar to the ratio between their valency numbers.

Mr. Redgrove further states that my hypothesis is wrong because two out of the four carbon links show considerably large values. It will be found that the formulæ applying to the olefins and acetylenes are respectively (*a*) M.H.C. $C_nH_{2n}| = | = 6n\,c + | = |$, and (*b*) M.H.C. $C_nH_{2n-2}|{\equiv}| = 6n\,c - 2c + |{\equiv}|$; $| = |$ and $|{\equiv}|$ representing additional heat values, which are constant. This is evident if we study a column (Column 11, Table I.) of so-called errors:—Olefins $| = |$, $-17{\cdot}2$, $18{\cdot}8$, $18{\cdot}9$; diolefins $| = |_2$, $-37{\cdot}3 = 2 \times 18{\cdot}65$; acetylenes $|{\equiv}|$, $-46{\cdot}2$, $46{\cdot}7$; diacetylenes $|{\equiv}|_2$, $-93{\cdot}9 = 2 \times -46{\cdot}95$. It is thus inadmissible to apply the relation $c = \frac{\text{M.H.C.}}{\text{Valency number}}$ to the above compounds, as Mr. Redgrove has done.

The additional heat values that have just been considered do not invalidate the valency rule, but constitute a peculiarity which calls for special explanation. Although characteristic of the $| = |$ and $|{\equiv}|$ links, they are by no means limited to these, for trimethylene, C_3H_6, which is incapable of reacting additively without a rupture of the ring, also possesses an additional heat value. The extra free energy of which the above is a sign may be supposed to give rise to intra-molecular tension, and also explains the extraordinary reactivity and instability of the compounds. They may in some cases be susceptible to spontaneous explosion—a fact which does not seem capable of explanation on any other hypothesis.

Finally, Mr. Redgrove obtains a mean value of $c = 26{\cdot}25$. I cannot obtain this number from the values given in Column 4, Table I.—I am, &c.,

GERVAISE LE BAS.

The Municipal School of Technology, Manchester.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Berichte der Deutschen Chemischen Gesellschaft. Vol. xl., No. 10, 1907.

Decomposition of Gaseous Hydrocarbons by Heating with Finely-divided Aluminium.—M. Kusnetzow.—When a dried hydrocarbon is led over a tube containing aluminium which is heated till it just begins to melt, it is found that the gaseous product of the reaction is almost pure hydrogen, while all the carbon is deposited in the tube. The author's experiments extended to methane, ethane, ethylene, and acetylene, which were obtained by the reduction of their haloid compounds. Thus aluminium decomposes the hydrocarbons into their elements, the hydrogen escaping in the free state, while the carbon is partly deposited mechanically upon the surface of the aluminium (and may be burnt to carbon dioxide by ignition in air), and partly forms a carbide which, when warmed gently with water, gives impure methane, among other hydrocarbons.

Action of Sodium Arsenite upon Sodium Ethyl Thiosulphate.—A. Gutmann.—When sodium arsenite acts upon sodium thiosulphate the latter is converted into sulphite and the arsenite into sodium monosulphoxyarsenate, $S_2O_3Na_2 + AsO_3Na_3 = Na_2SO_3 + AsSO_3Na_3$. It was therefore to be expected that if sodium ethyl thiosul-

phate was substituted for the thiosulphate, sodium ethyl sulphonate or sulphite, $SO_2(ONa)C_2H_5$ or $SO_2(Na)OC_2H_5$, would be obtained, according to the equation $S_2O_3NaC_2H_5 + AsO_3Na_3 = SO_3NaC_2H_5 + AsSO_3Na_3$. The author has, however, found that this reaction does not occur, for a strong smell of thioalkyl compound is produced. There are three possible explanations. The most obvious explanation would be the saponification of the sodium ethyl thiosulphate in presence of caustic soda, $S_2O_3NaC_2H_5 + NaOH$ $SO_4Na_2 + C_2H_5.SH$ or $H_2S_2O_3 = SO_3 + H_2S$, but no trace of sulphate was formed although mercaptan was present. Thus, this explanation could not be correct. The two remaining possibilities are represented by the equations—

$$2S_2O_3NaC_2H_5 + 2NaOH + AsO_3Na_3 = = 2SO_3Na_2 + C_2H_5S_2C_2H_5 + AsO_4Na_3 + H_2O$$

or—

$$2S_2O_3H_2 = 2SO_2 + S_2H_2 + O + OH_2,$$

and—

$$2S_2O_3NaC_2H_5 + 2NaOH + 2AsO_3Na_3 = = 2SO_3Na_2 + 2C_2H_5SH + 2AsO_4Na_3$$

or—

$$2S_2O_3H_2 = 2SO_2 + 2SH_2 + 2O.$$

When the reaction was investigated quantitatively it was found that the last equation represents the transformation which occurs, and the final products are sulphite, ethyl mercaptan, and tertiary sodium arsenate. It is very noteworthy that arsenate should be formed from a sulphite. The decomposition, $S_2O_3H_2 = SO_2 + SH_2 + O$, explains why, when sodium stannite acts upon sodium thiosulphate, no sulphate but black stannous sulphide is formed. The equation representing the reaction which occurs is—

$$2Sn(ONa)_2 + S_2O_3Na_2 + H_2O = = SnS + SO_3Na_2 + SnO_3Na_2 + 2NaOH.$$

Thus, thiosulphate undergoes the three reactions: — $S_2O_3H_2 = SO_2 + S + H_2O$, $S_2O_3H_2 = SO_3 + H_2S$, $S_2O_3H_2 = SO_2 + O + SH_2$.

Action of Ozone on Metallic Silver and Mercury.—W. Manchot and W. Kampschule.—The blackening of silver by means of ozone is most readily effected when the metal is first heated to incipient red heat. By a series of experiments in which the temperature of a silver tube was accurately fixed by boiling a pure liquid of known boiling-point in it, the effects at different temperatures were studied. At 100° a milk-white deposit is formed; at 154° a dark blue or steel-blue film appears; and between 220° and 240° the action is most marked. Above this temperature it becomes feebler, and at 450° no change is perceptible. These experiments were carried out with carefully dried ozone. With damp ozone the same results were obtained, but all these statements hold good only if the surface of the silver is quite clean. The authors find that the blackening of silver in the cold even by very dilute ozone is due to the presence on its surface of very minute quantities of some substance such as oxide of silver, cobalt, nickel, &c., which acts as a catalytic oxygen carrier. Even when the metal is heated to redness traces of oxide remain on its surface. Mercury behaves in the same way as silver towards ozone. The effect first increases, and then decreases, and finally disappears, though the temperature intervals in which the changes take place are somewhat lower.

Products of Dehydration of Dichloro-chromic Chloride.—Neils Bjerrum.—When green chromic chloride, $CrCl_3.6H_2O$, is allowed to stand over phosphorus pentoxide in a vacuum of 1 mm. for twenty days, it yields a red modification, probably with one and a-half molecules of water, or possibly its formula is $CrCl_3.2H_2O$, and it slowly gives up water. This new modification is very deliquescent, giving a greenish yellow solution with water, which turns blue-violet on standing. The electric conductivity of the salt at 25° is smaller than that of a solution of the green chloride, but very rapidly rises. The solution therefore probably contains less chlorine in the form of chlorine ions than a solution of dichloro-chromic chloride, and the splitting off of water from the tetrahydrate is not accompanied by a deep-seated change in the constitution of the salt. When dehydrated at a higher temperature in a current of chlorine, five and a-half molecules of water escape, and a red substance is left. At 0° this substance is rapidly and apparently completely dissolved, giving a red solution, but after a short time a red precipitate separates, which again dissolves after standing for a day. Probably the chromic chloride is converted by heating into the colloidal form, which first dissolves, but is precipitated if the solution possesses a certain amount of salting out electrolyte formed owing to the change of the chloride.

Heat of Formation of Phosphorus Nitride, P_3N_5.—Alfred Stock and Franz Wrede.—The authors employed a Krœker's bomb with a platinum resistance thermometer to determine the heat of combustion of phosphorus nitride. The bomb was lined with enamel, and a porcelain crucible was used, while the platinum lining of the lid was protected by mica. When the nitride burns phosphorus pentoxide is formed, as well as free nitrogen, and fills the whole bulb with a white mist, taking up any water present. This reaction takes some time and much heat is developed, so that it is necessary to determine accurately the water present, or it is better to perform the combustion in perfectly dry oxygen. The nitrogen which is oxidised cannot be estimated as nitric acid, but the resulting nitric oxide has to be determined by another method. The authors condensed the gaseous contents of the bomb in liquid air, and allowed the oxygen to boil away. The nitric oxide remained behind quantitatively, and was vaporised by heating and receiving it into titrated caustic potash. It was thus found that for 1 grm.-mol. of P_3N_5 (163 grms.) the heat of combustion at constant temperature is 473·2 cals. and at constant pressure 474·7 cals. These figures relate to the decomposition of the nitride to P_2O_5 and N. To calculate the heat of formation of P_3N_5 it is necessary to determine the difference between the heats of combustion of free phosphorus and P_3N_5. The results are as follows:—

For Colourless Phosphorus—

Heat of combustion of	P to P_2O_5	$= 3 \times 370{\cdot}8 =$	1112·4 cals.
	P_3N_5	$= -2 \times 474{\cdot}7 =$	949·4 „
		$2P_3N_5 =$	163·0 „

Therefore, heat of formation of P_3N_5 = +81·5 cals.

For Red Phosphorus—

Heat of combustion	P to P_2O_5	$= 3 \times 363{\cdot}4 =$	1090·2 cals.
	P_3N_5	$= -2 \times 474{\cdot}7 =$	949·4 „
		$2P_3N_5 =$	140·8 „

Therefore, heat of formation of P_3N_5 = 70·4 cals.

Preparation and Properties of Fluorides of Hexavalent Molybdenum.—Otto Ruff and Fritz Eisner.—Molybdenum hexafluoride may be prepared by allowing molybdenum pentachloride and anhydrous hydrofluoric acid to act upon one another at about 30—40°, or by the addition of bromine and antimony pentafluoride to the pentachloride. To obtain it in the pure state it is best to allow pure fluorine to act on metallic molybdenum. It is a soft crystalline mass, melting at 17° to a colourless liquid which boils at 35°. Its colourless vapour gives a blue-white mist in air. It is very sensitive to moisture and decomposes with a little water giving blue molybdenum oxides. With much water it gives a colourless solution. It does not decolorise permanganate, but is easily and completely absorbed by ammonia and alkalis. With alkali fluorides it forms double compounds. The oxytetrafluoride, $MoOF_4$, results when molybdenum oxytetrachloride is treated with anhydrous hydrofluoric acid. It is a white very hygroscopic solid at ordinary temperatures, becoming blue, and deliquescing in the air. It melts at 97—98° and boils at about 180°, and its density at the temperature of the room is 3·001. It gives a colourless solution with water and alcohol, and light-green or yellow

solutions with ether and chloroform; when the aqueous solution is evaporated molybdenum trioxide is deposited, while a white mass is left when the other solutions are evaporated. It is insoluble in toluene, almost insoluble in benzene and carbon disulphide; it gives a colourless solution with concentrated sulphuric acid, hydrofluoric acid being evolved. With phosphorus trichloride and oxychloride, arsenic trichloride, and sulphur monochloride it gives brown solutions. Molybdenum dioxydifluoride is formed when molybdenum trioxide is ignited with fluorides, *e.g.*, lead fluoride or kryolite, or when anhydrous hydrofluoric acid reacts with molybdenum dioxydichloride. It is a white hygroscopic solid like the oxytetrafluoride, turning green in air and deliquescing. It sublimes at 265—270°, and its density is 3·494. It gives a blue solution with a little water, and a colourless solution with much water. It is almost insoluble in ether, chloroform, and carbon tetrachloride, and completely insoluble in toluene. It dissolves to a colourless solution in arsenic trichloride, silicon tetrachloride, and sulphuryl chloride, and gives a blue solution with phosphorus trichloride. All these solutions on warming evolve gases. The reactions of the dioxydifluoride and oxytetrafluoride resemble those of the hexafluoride, but are less energetic. The comparison of the physical properties of the new fluorides with those of the corresponding compounds of tungsten illustrate the close connection between these two elements.

Electrolytic Dissociation of Fused Salts.—K. Arndt.—The calculation of the degree of dissociation of a dissolved electrolyte is performed according to Arrhenius's theory by comparing the conductivity of the solution with the limiting value to which its equivalent conductivity approaches as the dilution increases. This method could not be applied to fused salts because no solvent was known which did not conduct the electric current. The author has discovered that boric acid anhydride may be employed as such a solvent, for its conductivity for the purest Kahlbaum's preparation is only $K = 0{\cdot}000021$ at 900°, *i.e.*, it conducts as badly as distilled water. He used sodium metaphosphate as dissolved electrolyte, and measured the viscosity and conductivity at 900° with different percentages of the electrolyte in the melt. He found that the product conductivity × viscosity is constant, and thus the conductitity is proportional to the viscosity. Calculated for the same viscosity the equivalent conductivity is independent of the concentration. This surprising result is most simply explained by assuming that the fused sodium metaphosphate is completely dissociated. The same may hold good for potassium and sodium chlorides and other salts, and the assumption is supported by the fact that with all these salts the increase of conductivity with the temperature is represented by a straight line, which points to a simple constitution of the melts. The salts of divalent metals, *e,g.*, calcium chloride, give a conductivity curve, which first rises rapidly and then more gradually with the temperature, and finally approximates to a straight line. Hence it may be supposed that the dissociation is not complete at the melting-point, and that the salt is not completely split up till the temperature is further raised. This conclusion that fused monovalent salts are completely dissociated is confirmed by some work of Lorenz, which has not yet been published.

Ammonium Amalgam.—George McPhail Smith.—The author's experiments have shown that Le Blanc's conclusion that ammonium amalgam is a compound of mercury with the metallic radicle NH_4 is the correct view of its constitution, and that the assumptions of Moissan that it is a compound of ammonia and mercury hydride, and of Rich and Travers that it is free ammonium dissolved in mercury, are both untenable. Moissan based his view upon the fact that sodium amalgam containing sodium hydride reacts with aqueous ammonia with increase of volume, while sodium amalgam alone gives hydrogen at constant volume with the same liquid. The author repeated Moissan's experiments with some modifications, and found that although sodium amalgam does not increase in volume with aqueous ammonia, other amalgams do, and sodium amalgam itself swells up with ammonium salt solutions. Also at a lower temperature the NH_4 of the ammonium hydroxide present in the solution is capable of expelling sodium from its amalgam. Moreover, it has been found that in the form of their amalgams the alkali and alkaline earth metals are mutually replaceable, and since ammonium amalgam also possesses this property it must be regarded as a true analogue of potassium amalgam. There is no ground for Rich and Travers's assumption that ammonium amalgam is a simple solution of free ammonia in metallic mercury, and their experiments only show that the general formula of the amalgam is NH_4Hg_m. Cryoscopic measurements cannot determine m, and there is no reason for thinking that it is equal to o. Indeed, Moissan and Ruff's failure to isolate free ammonium at very low temperatures argues against this assumption. The author's experiments all go to show that ammonium amalgam is a compound of the formula $MeHg_m$, dissolved in free mercury. This compound, NH_4Hg_m, is very unstable; at o° it decomposes slowly, and more quickly at room temperature into hydrogen, ammonia, and mercnry. The gases are retained by the mass, and cause the characteristic swelling up, which, however, is not a property of the original compound, but is only an incidental phenomenon of its decomposition.

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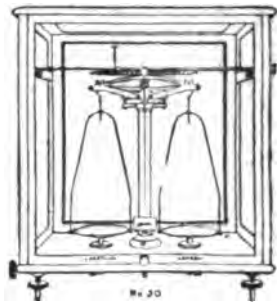

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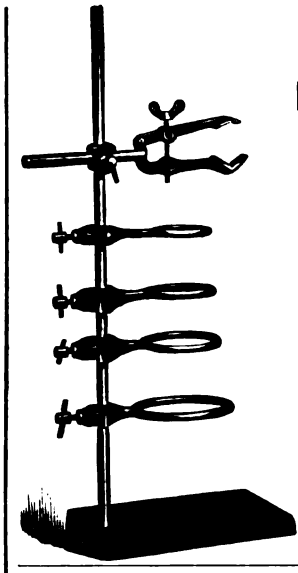

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INAUGURAL ADDRESS OF THE PRESIDENT,

Sir David Gill, K.C.B., LL.D., D.Sc., F.R.S., Hon. F.R.S.E., &c.

(Concluded from p. 55).

The Density of Stellar Distribution at Different Distances from our Sun.

Consider, lastly, the distribution of stellar density, that is, the number of stars contained in the unit of volume.

We cannot determine *absolute* star-density, because, for example, some of the stars which we know from their measured parallaxes to be comparatively near to us are in themselves so little luminous that if removed to even a few light-years greater distance they would appear fainter than the ninth magnitude, and so fall below the magnitude at which our data at present stop.

But if we assume that intrinsically faint and bright stars are distributed in the same proportion in space, it will be evident that the comparative richness of stars in any part of the system will be the same as the comparative richness of the same part of the system in stars of a particular luminosity. Therefore, as we have already found the arrangement in space of the stars of different degrees of luminosity, and consequently their number at different distances from the Sun, we must also be able to determine their relative density for these different distances.

Kapteyn finds in this way that, starting from the Sun, the star-density (*i.e.*, the number of stars per unit volume of space) is pretty constant till we reach a distance of some 200 light-years. Thence the density gradually diminishes till, at about 2500 light-years, it is only about *one-fifth* of the density in the neighbourhood of the Sun (*Publications Astron. Lab. Groningen*, No. 11). This conclusion must, however, be regarded as uncertain until we have by independent means been enabled to estimate the absorption of light in its course through interstellar space, and obtained proof that the ratio of intrinsically faint to bright stars is constant throughout the universe.

Thus far Kapteyn's researches deal with the stellar universe as a whole; the results, therefore, represent only the *mean* conditions of the system. The further development of our knowledge demands a like study applied to the several portions of the universe separately. This will require much more extensive material than we at present possess.

As a first further approximation the investigation will have to be applied separately to the Milky Way and the parts of the sky of higher galactic latitude. The velocity and direction of the Sun's motion in space may certainly be treated as constants for many centuries to come, and these constants may be separately determined from groups of stars of various regions, various magnitudes, various proper motions, and various spectral types. If these constants as thus separately determined are different, the differences which are not attributable to errors of observation must be due to a common velocity or direction of motion of the group or class of star to which the Sun's velocity or direction is referred. Thus, for example, the Sun's velocity as determined by spectroscopic observations of motion in the line of sight, appears to be sensibly smaller than that derived from fainter stars. The explanation appears to be that certain of the brighter stars form part of a cluster or group of which the Sun is a member, and these stars tend to some extent to travel together. For these researches the existing material, especially that of the determination of velocities in the line of sight, is far too scanty.

Kapteyn has found that stars whose proper motions exceed 0·05″ are not more numerous in the Milky Way than in other parts of the sky (*Verl. Kn. Akad. Amsterdam*, January, 1893); in other words, if only the stars having proper motions of 0·05″ or upwards were mapped there would be no aggregation of stars showing the existence of a Milky Way.

The proper motions of stars of the second spectral type are, as a rule, considerably larger than those of the first type; but Kapteyn comes to the conclusion that this difference does not mean a real difference of velocity, but only that the second-type stars have a smaller luminosity, the mean difference between the two types amounting to 2½ magnitudes (*Verl. Kn. Akad. Amsterdam*, April, 1892).

The Future Course of Research.

In the last Address delivered from this Chair on an astronomical subject, Sir William Huggins, in 1891, dealt so fully with the chemistry of the stars that it seemed fitting on the present occasion to consider more especially the problem of their motion and distribution in space, as it is in this direction that the most striking advances in our knowledge have recently been made. It is true that since 1891 great advances have also been made in our detailed knowledge of the chemistry of the Sun and Stars. The methods of astro-spectrography have been greatly improved, the precision of the determination of motion in the line of sight greatly enhanced, and many discoveries made of those close double stars, ordinarily termed spectroscopic doubles, the study of which seems destined to throw illustrative light upon the probable history of the development of systems from the original nebular condition to that of more permanent systems.

But the limitations of available time prevent me from entering more fully into this tempting field, more especially as it seems desirable, in the light of what has been said, to indicate the directions in which some of the astronomical work of the future may be most properly systematised. There are two aspects from which this question may be viewed. The first is the more or less immediate extension of knowledge or discovery; the second the fulfilment of our duty, as astronomers, to future generations. These two aspects should never be entirely separated. The first, as it opens out new vistas of research and improved methods of work, must often serve as a guide to the objects of the second. But the second is to the astronomer the supreme duty, viz., to secure for future generations those data the value of which grows by time.

As the result of the Congress of Astronomers held at Paris in 1887 some sixteen of the principal observatories in the world are engaged, as is well known, in the laborious task, not only of photographing the heavens, but of measuring these photographs and publishing the *relative* positions of the stars on the plates down to the eleventh magnitude. A century hence this great work will have to be repeated, and then, if we of the present day have done our duty thoroughly, our successors will have the data for an infinitely more complete and thorough discussion of the motions of the sidereal system than any that can be attempted to-day. But there is still needed the accurate meridian observation of some eight or ten stars on each photographic plate, so as to permit the conversion of the *relative* star-places on the plate into *absolute* star-places in the heavens. It is true that some of the astronomers have already made these observations for the reference stars of the zones which they have undertaken. But this seems to be hardly enough. In order to co-ordinate these zones, as well as to give an accuracy to the *absolute* positions of the reference stars corresponding with that of the *relative*

positions, it is desirable that this should be done for *all* the reference stars in the sky by several observatories. The observations of well-distributed stars by Kustner at Bonn present an admirable instance of the manner in which the work should be done. Several observatories in each hemisphere should devote themselves to this work, employing the same or other equally efficient means for the elimination of sources of systematic error depending on magnitude, &c., and it is of far more importance that we should have, say, two or three observations of each star at three different observatories than two or three times as many observations of each star made at a single observatory.

The southern cannot boast of a richness of instrumental and personal equipment comparable with that of the northern hemisphere, and consequently one welcomes with enthusiasm the proposal on the part of the Carnegie Institute to establish a meridian observatory in a suitable situation in the southern hemisphere. Such an observatory, energetically worked, with due attention to all necessary precautions for the exclusion of systematic errors would conduce more than anything else to remedy in some degree that want of balance of astronomical effort in the two hemispheres to which allusion has already been made. But in designing the programme of the work it should be borne in mind that the proper duty of the meridian instrument in the present day is no longer to determine the positions of all stars down to a given order of magnitude, but to determine the positions of stars which are geometrically best situated, and of the most suitable magnitude for measurement on photographic plates, and to connect these with the fundamental stars. For this purpose the working list of such an observatory should include only the fundamental stars and the stars which have been used as reference stars for the photographic plates.

Such a task undertaken by the Carnegie Observatory, by the Cape, and if possible by another observatory in the southern hemisphere, and by three observatories in the northern, would be regarded by astronomers of the future as the most valuable contribution that could be made to astronomy of the present day. Taken in conjunction with the astrographic survey of the heavens now so far advanced, it is an opportunity that if lost can never be made good; a work that would grow in value year by year as time rolls on, and one that would ever be remembered with gratitude by the astronomers of the future.

But for the solution of the riddle of the universe much more is required. Besides the proper motions, which would be derived from the data just described, we need for an ideal solution to know the velocity in the line of sight, the parallax, the magnitude, and the spectrum-type of every star.

The broad distinction between these latter data and the determination of proper motion is this, that whereas the observations for proper motion increase in value as the square of their age, those for velocity in the line of sight, parallax, magnitude, and type of spectrum may, for the broader purposes of cosmical research, be made at any time without loss of value. We should therefore be most careful not to sacrifice the interests of the future by immediate neglect of the former for the latter lines of research. The point is that those observatories which undertake this meridian work should set about it with the least possible delay, and prosecute the programme to the end with all possible zeal. Three observatories in each hemisphere should be sufficient; the quality of the work should be of the best, and quality should not be sacrificed for speed of work.

But the sole prosecution of routine labour, however high the ultimate object, would hardly be a healthy condition for the astronomy of the immediate future. The sense of progress is essential to healthy growth, the desire to know must in some measure be gratified. We have to test the work that we have done in order to be sure that we are working on the right lines, and new facts, new discoveries, are the best incentives to work.

For these reasons Kapteyn, in consultation with his colleagues in different parts of the world, has proposed a scheme of research which is designed to afford within a comparatively limited time a great augmentation of our knowledge. The principle on which his programme is based is that adequate data as to the proper motions, parallaxes, magnitudes, and the type of spectrum of stars situated in limited but symmetrically distributed areas of the sky, will suffice to determine many of the broader facts of the constitution of the universe. His proposals and methods are known to astronomers, and need not therefore be here repeated. In all respects save one these proposals are practical and adequate, and the required co-operation may be said to be already secured—the exception is that of the determination of motion in the line of sight.

All present experience goes to show that there is no known satisfactory method of determining radial velocity of stars by wholesale methods, but that such velocities must be determined star by star. For the fainter stars huge telescopes and spectroscopes of comparatively low dispersion must be employed. On this account there is great need in both hemispheres of a huge reflecting telescope—six to eight feet in aperature—devoted almost exclusively to this research. Such a telescope is already in preparation at Mount Wilson, in America, for use in the northern hemisphere. Let us hope that Professor Pickering's appeal for a large reflector to be mounted in the southern hemisphere will meet with an adequate response, and that it will be devoted there to this all-important work.

Conclusion.

The ancient philosophers were confident in the adequacy of their intellectual powers alone to determine the laws of human thought, and regulate the actions of their fellow men, and they did not hesitate to employ the same unsupported means for the solution of the riddle of the universe. Every school of philosophy was agreed that some object which they could see was a fixed centre of the universe, and the battle was fought as to what that centre was. The absence of facts, their entire ignorance of methods of exact measurement, did not daunt them, and the question furnished them a subject of dispute and fruitless occupation for twenty-five centuries.

But astronomers now recognise that Bradley's meridian observations at Greenwich, made only 150 years ago, have contributed more to the advancement of sidereal astronomy than all the speculations of preceding centuries. They have learned the lesson that human knowledge in the slowly developing phenomena of sidereal astronomy must be content to progress by the accumulating labours of successive generations of men; that progress will be measured for generations yet to come more by the amount of honest, well-directed, and systematically discussed observation than by the most brilliant speculation; and that, in observation, concentrated systematic effort on a special thoughtfully selected problem will be of more avail than the most brilliant but disconnected work.

By these means we shall learn more and more of the wonders that surround us, and recognise our limitations when measurement and facts fail us.

Huggins's spectroscope has shown that many nebulæ are not stars at all; that many well-condensed nebulæ, as well as vast patches of nebulous light in the sky, are but inchoate masses of luminous gas. Evidence upon evidence has accumulated to show that such nebulæ consist of the matter out of which stars (*i.e.*, suns) have been and are being evolved. The different types of star spectra form such a complete and gradual sequence (from simple spectra resembling those of nebulæ onwards through types of gradually increasing complexity) as to suggest that we have before us, written in the cryptograms of these spectra, the complete story of the evolution of suns from the inchoate nebula onwards to the most active sun (like our own), and then downward to the almost heatless and invisible ball. The period during which human life has existed on our globe is probably too short—even if our first parents had begun the work—to afford observational proof of such a

cycle of change in any particular star; but the fact of such evolution, with the evidence before us, can hardly be doubted. I most fully believe that, when the modifications of terrestrial spectra under sufficiently varied conditions of temperature, pressure, and environment have been further studied, this conclusion will be greatly strengthened. But in this study we must have regard also to the spectra of the stars themselves. The stars are the crucibles of the Creator. There we see matter under conditions of temperature and pressure and environment, the variety of which we cannot hope to emulate in our laboratories, and on a scale of magnitude beside which the proportion of our greatest experiment is less than that of the drop to the ocean. The spectroscopic astronomer has to thank the physicist and the chemist for the foundation of his science, but the time is coming—we almost see it now—when the astronomer will repay the depth by wide-reaching contributions to the very fundamenta of chemical science.

By patient, long-continued labour in the minute sifting of numerical results, the grand discovery has been made that a great part of space, so far as we have visible knowledge of it, is occupied by two majestic streams of stars travelling in opposite directions. Accurate and minute measurement has given us some certain knowledge as to the distances of the stars within a certain limited portion of space, and in the cryptograms of their spectra has been deciphered the amazing truth that the stars of both streams are alike in design, alike in chemical constitution, and alike in process of development.

But whence have come the two vast streams of matter out of which have been evolved these stars that now move through space in such majestic procession?

The hundreds of millions of stars that comprise these streams, are they the sole ponderable occupants of space? However vast may be the system to which they belong, that system itself is but a speck in illimitable space; may it not be but one of millions of such systems that pervade the infinite?

We do not know.

"Canst thou by searching find out God? Canst thou find out the Almighty unto perfection?"

ADDRESS TO THE CHEMICAL SECTION OF THE BRITISH ASSOCIATION.

LEICESTER, 1907.

By Professor A. SMITHELLS, B.Sc., F.R.S., President of the Section.

THE year which has elapsed since the meeting of our Section at York has been eventful in the most melancholy of ways; the losses sustained by our science have been unparalleled. The passing bell seems to have tolled almost without intermission as one after another of our masters have been taken from us: in Russia, Mendeleeff, Menschutkin, and Beilstein; in France, Berthelot and Moissan; in Holland, Bakhuis-Roozeboom. Whilst in some of these cases we may find consolation in contemplating a length of life and sustained activity beyond what we might have dared to expect, in others our regret is increased by the sense of untimeliness and of vanished hopes. I am tempted to speak of the work of such mighty men as Berthelot and Mendeleeff, to dwell upon the discoveries by which they transformed the whole fabric of chemical science; but this is not the occasion on which to offer an estimate of the labours of those who have passed away. I can only say that in the bond of brotherhood which the pursuit of science establishes among the different nations of the earth we who are Englishmen feel and deplore these losses as our own.

I must not omit to allude also, as I do with deep regret, to the death in our own country of two such ardent and fruitful workers as Cornelius O'Sullivan and Robert Warington.

These words were already in print when again we were called to mourn the loss of one of our greatest men, one who but a year ago was the subject of our special rejoicings, and whose vigour of body and youthfulness of spirit seemed to promise the long continuance of a noble and an extraordinarily fruitful life. We can at least feel thankful that William Henry Perkin lived long enough to learn in what honour and esteem his name was held, not only among his countrymen, but by all the chemists of the world, and by the leaders of those great industries of which he was justly acclaimed the founder. For more than a generation Sir William Perkin had been one of the most familiar figures at the meetings of this Section, and greatly shall we miss his gentle presence, his wise counsel, and his valued contributions.

I can, perhaps, best occupy your time to-day by attempting to give some account of the present state of the scientific subject to which I have paid most attention. The topic of flame, after a long period of repose, has aroused much interest during late years, and I think we may say that some considerable progress has been made in its elucidation, although in this, as in all other subjects of scientific inquiry, the more closely we scrutinise it the more impressed must we be with what still remains unknown.

One of the first questions that meet us in the study of flame is that of the temperature at which in any given case the phenomenon becomes evident. Here, I think, a great clarification of view has taken place. The old idea that there existed a fixed temperature at which inflammation suddenly took place cannot now be maintained, and the term "ignition temperature" has acquired a different meaning. It is now known that in a very great number of cases a mixture of two flame-forming gases, when gradually raised in temperature, will develop luminosity quite gradually, *pari passu*, with the chemical combination that is being induced. This phenomenon is, of course, known universally in connection with phosphorus, but it is not so widely known in connection with other combustible substances. There are some simple facts that seem as if they never could gain admission to text-books, and I do not think I have known more than a single chemical book that is not likely to leave a student under the impression that the phosphorescence of phosphorus is an almost unique phenomenon. I do not know how many times the independent discovery has been made that sulphur, arsenic, carbon disulphide, alcohol, ether, paraffin, and a whole host of other compounds, inorganic and organic, will phosphoresce as truly as phosphorus itself; that, in fact, phosphorescent combustion is the normal phenomenon antecedent to what we ordinarily call flame.

This is, after all, only in harmony with the general truth that chemical combination between two gases does not set in suddenly, but comes into evidence quite gradually as the temperature is raised from a point at which the action, if it occurs at all, is so slow as to be negligible. The increase in the rate of combination is, of course, very rapid as compared with the increase of temperature, a difference of about 10° C. serving to double it. The interval between the beginning of phosphorescence and the production of vigorous flames may therefore be very short. In the case of phosphorus this interval, being from 7° to 60° C., includes ordinary atmospheric temperatures; hence the phosphorescence of phosphorus is a phenomenon that could not well be overlooked. If the prevailing terrestrial temperature were below 7° C., at which, under normal air-pressure, the phosphorescence of phosphorus ceases, it is possible that this element might never have acquired its peculiar reputation; it would not have shown in the dark, and in lighting it with a taper the phosphorescent interval would have been passed over as quickly as is ordinarily the case in the ignition of sulphur, paraffin, and other common combustibles. To make phosphorescence apparent in these last cases it is necessary to take special care to heat up a mixture of the combustible gas and air gently, and to maintain it at a temperature approaching,

but not quite reaching, that of ignition. There is no simpler way than that used by Sir William Perkin, who brought the combustible substance near to, or in contact with, a massive metal ball previously heated to the suitable temperature.

The change from phosphorescence to ordinary flame is not sudden, but the appearance of ordinary flame is the end point of a continuous, though rapid, development. This end point is the temperature of ignition. What, then, determines the temperature of ignition? The answer to this question has been given with characteristic conciseness by van 't Hoff as "the temperature at which the initial loss of heat due to conduction, &c., is equal to the heat evolved in the same time by the chemical reaction."

We may obtain a clear idea of the meaning of temperature of ignition by supposing a combustible mixture of gases such as that of air and the vapour of carbon disulphide to issue through an orifice into an indifferent atmosphere. If we surround the orifice by a ring of platinum wire, which is gradually heated up by a current of electricity, a flame will gradually make its appearance. If, as soon as this is observed, the heating of the wire by the current be discontinued, the flame will disappear; it is, in fact, not self-supporting, but depends on the accessory supply of heat through the electrically heated wire. If now we raise the ring to a higher temperature we shall get a brighter flame, owing to an increased rate of chemical action, and at last we shall reach a point where it is possible to cut off the electric current without causing at the same time the extinction of the flame. This is the true temperature of ignition, the temperature at which the reaction proceeds at a rate just sufficient to overbalance the loss of heat by radiation, conduction, and convection from the burning layer of gases, so that the next layer is put in the same state, and steady combustion proceeds.

Phosphorescence has been spoken of as degraded combustion, and, though literally the appellation is correct, I think it is liable to be misunderstood. Again, it is often supposed that phosphorescence is necessarily associated with the formation of incompletely oxidised products. This may be the case in a chemical system which is capable of affording different products at different temperatures, but it is not an essential feature; the phosphorescent combustion of sulphur, for example, affords nothing but sulphur dioxide.

Temperature of ignition is, then, neither a temperature at which combination suddenly begins nor one dependent solely on the nature of the combining gases. It will vary with the proportion in which the gases are mixed and with their pressure and other circumstances. Notwithstanding the simplicity of this conception, it must be admitted that there are many obscure facts connected with the ignition of gases. The inflammability of gaseous mixtures is not necessarily greatest when they are mixed in the proportions theoretically required for complete combination; the influence of foreign gases does not appear to follow any simple law; the presence of a very small quantity of a foreign gas may exercise a profound influence on the ignition temperature as in the case of the addition of ethylene to hydrogen. When a mixture of methane and air is raised to its ignition temperature, a sensible interval (about ten seconds) elapses before inflammation occurs. These facts are cognate to others which have increased upon us so abundantly in connection with the influence of moisture on chemical change. The study of the oxidation of phosphorus in particular brings us among rocks and shoals. Apart from the influence of moisture on the combination we have the limitation of the process by a certain tension of oxygen and by minute quantities of a vast number of chemical substances, among which, in spite of much labour, no other common bond can be found. We do not know what oxide is initially formed in the oxidation, and the existence of the oxides P_4O and P_2O is as confidently disputed as it is affirmed. There is some reason for believing that the phosphorescence connected with phosphorus succeeds the formation of one oxide and accompanies the formation of another. The state of the oxygen, whether atomic, ionic, or molecular, which acts on phosphorus, the induced oxidation of other substances, the ionisation of air accompanying the oxidation—these are all matters concerning which there exists a bewildering literature that hangs over us like a cloud. The whole of my Address would, in fact, not suffice for a summary of the state of our ignorance about the oxidation of phosphorus. The subject, simple as it appears at first sight, is really involved with a vast number of unsolved chemical problems the elucidation of which would throw much light on chemical action in general. I may, perhaps, bequeath the topic to some successor in this Chair as one which may serve to illustrate the advance of knowledge since these present days of darkness.

The structure of flames has always been regarded as dependent upon the chemical changes taking place in the differentiated regions, but until recent times little attention has been given to any question beyond the cause of the bright luminosity of hydrocarbon flames. In a flame such as that of hydrogen or carbon monoxide, where we have some reason to suppose that the same kind of chemical transaction is taking place throughout the region of combustion, we should not expect to find a differentiation of structure, and, as a matter of fact, we do not find any. Erroneous ideas have gained currency from the use of impure gases, and hydrogen is still described as burning with a pale blue flame, although Stas long ago stated that if the gas is highly purified, and the air freed from dust, the flame even in a dark room can only be discovered by feeling for it; a fact consistent with the line spectrum of water lying wholly in the ultra-violet. The presence of a very small quantity of free oxygen in carbon monoxide destroys the perfect simplicity of the single shell of blue flame with which the purified gas burns, and in other flames small quantities of gaseous impurities or of atmospheric dust give rise to features of structure and halos which have been frequently supposed to pertain to the flame of the combiniug gases. The fringe of a flame in air may be often tinged by the presence of oxides of nitrogen.

No flame better illustrates the relation of structure to chemical processes than that of cyanogen, where the two steps in the oxidation of the carbon are clearly marked out in colour. Apart from hydrocarbon flames, very few others have been carefully explored from this point of view. There is, unfortunately, no gas composed of two combustible gaseous elements; and, though such gases as the hydrides of phosphorus and sulphur do not fall far short of this, the experimental difficulties of an exact exploration of their flames are very great. We are thus prevented from studying the flame of a composite combustible in its simplest form.

The flames of hydrocarbons have naturally been the subject of most frequent investigation. The use of single hydrocarbons instead of the mixtures present in coal-gas and other common combustibles has simplified the study considerably. Two problems stand out prominently: one is to trace the steps in the oxidation of the hydrocarbon, the other to account for the bright patch of yellow luminosity. With regard to the question of the luminosity, I do not think there is any longer doubt about its being due essentially to the separation within the flame of minute solid particles of what is practically carbon. The separation seems to be adequately explained by the high temperature of the blue burning walls of the flame, which decomposes the unburned hydrocarbon within. In a similar way arsenic and sulphur and phosphorus are liberated within flames of their hydrides; but these elements, being volatile, do not appear as solids unless a cold object be placed within the flame. In the case of the hydride of silicon the liberated element at once oxidises to form the solid non-volatile oxide, which gives a bright glow.

The mode in which a hydrocarbon yields carbon by the application of a high temperature has been the subject of

experiment and of hypothesis; but neither the view of Berthelot, that the carbon results from a continuous coalescence of hydrocarbon molecules with elimination of hydrogen, nor that of Lewes, according to which the formation and sudden decomposition of acetylene is the essence of the phenomenon, appears to me to be in harmony with the experimental facts; and I am not aware that either view has secured any support from other workers in this field. It is certainly not easy to ascertain experimentally the changes undergone by a single hydrocarbon as its temperature is raised, and at the last it may be objected that the course of events in contact with the solid walls of a containing vessel is not necessarily the same as that within the gaseous envelope of a flame. I am glad to think that there is promise of further light on this subject from the work of Professor Bone.

The course of oxidation of hydrocarbons has been the subject of very careful and fruitful study. The old view that a selective or preferential oxidation of the hydrogen always took place, that with a restricted supply of oxygen the hydrogen was oxidised and the carbon set free, is, I think, no longer maintained by anyone who has studied the question. The explosion of ethylene with its own volume of oxygen, which leaves us with practically all the carbon oxidised and all the hydrogen free, is fatal to this view. Again, when hydrocarbons are burned in a flame with a restricted supply of air, as is the case in the inner cone of the flame of a well-aërated Bunsen burner, there is clearly no separation of solid carbon, and the products of combustion when withdrawn and analysed disclose the presence of much free hydrogen and no unoxidised carbon. In describing this experimental fact I have spoken of it as the preferential oxidation of carbon. I have always thought it pedantic to quarrel with that expression; for, in speaking of a chemical transaction, we usually include only a description of the initial and final states of combination. I should be sorry, however, to detach the expression from the facts it describes and to exalt it into a general doctrine. That would be quite inadmissible, and, if there is any danger of misunderstanding, it would be better to avoid using the expression.

The admirable researches carried out in the University of Manchester by Professor Bone and his collaborators have afforded most valuable information as to the oxidation of hydrocarbons at temperatures extending from those of incipient oxidation up to the highest ones that prevail in a flame. According to Professor Bone, the oxidation of a hydrocarbon involves nothing in the nature of a selective or preferential oxidation of the carbon or the hydrogen; but it occurs in several well-defined stages, during which oxygen enters into and is incorporated with the hydrocarbon molecule, forming oxygenated intermediate products, among which are alcohols and aldehydes. The reaction, just referred to, between ethylene and an equal volume of oxygen is, according to Professor Bone, to be represented by the scheme :—

$$\begin{matrix} CH_2 & & CH.OH & & CH.OH & & H_2C{:}O & & H_2{+}CO \\ \vdots & \rightarrow & \vdots & \rightarrow & \vdots & \rightarrow & & \rightarrow & \\ CH_2 & & CH_2 & & CH.OH & & H_2C{:}O & & H_2{+}CO \end{matrix}.$$

There can be no question about the facts on which this scheme is based, and they are a new and important addition to knowledge.

It is a great aid to the study of chemical changes, when we can resolve them into stages, whether or not these stages be realisable under certain experimental conditions. In this way we can get a clear view of the relationship between the action under one set of circumstances to the action under another set; and in this way also we can often establish rational links between reactions which at first sight seem quite disconnected. Intermediate reactions are much used to elucidate cases of contact action, and in the processes of organic chemistry they are almost universally assumed.

I am far from wishing to disparage these practices, but I think it important that we should realise how far we are dealing with convenient devices, and how far with ascertained facts. The isolation of an intermediate product under one set of circumstances is in itself no proof that this product is transitorily formed when the reaction is proceeding under another set of circumstances; and if we were to assume generally that because we can represent a chemical transaction as if it were due to a successive construction and destruction of a series of molecular edifices it actually does take such a course, we should, I think, be making the same kind of mistake as to suppose that in the application of two differently directed forces to a body at rest, the body will move successively in the direction of each force instead of moving immediately in the direction of their resultant. I know that I may be considered hypercritical, and perhaps obstinate, in this matter; but I wished to state the reasons that prevent me from accepting entirely the interpretation which Professor Bone has given to his experimental results, and to draw attention to a question of general importance that has not, I think, received the attention it deserves.

The mode of burning of carbon, whether in the free state or as a constituent of a compound, is not at all easy to determine; and notwithstanding many investigations, among which must be specially mentioned those of Professor H. B. Dixon and his collaborators, so simple-looking a question as whether carbon forms carbon monoxide by directly uniting with oxygen, or only by reducing carbon dioxide, is still a matter of uncertainty.

Our knowledge concerning the question of flame temperatures has been much improved in recent times, thanks mainly to the admirable work of M. Le Chatelier. The well-known memoir of Mallard and Le Chatelier on the explosion of gases supplied the data which first permitted of a moderately exact calculation of flame temperatures, and the perfection of the thermo-couple by M. Le Chatelier gave us the first instrument that could be used directly for making a satisfactory measurement. The uncertainty connected with this subject may be well illustrated by quoting the temperatures that have at different times been ascribed to the flame of coal-gas when burnt in a Bunsen burner, where we have had values varying from 1230° to 2350° C.

The question of calculating the temperature attained during combustion by reference to calorimetric values, specific heat, dissociation, and other considerations is to form the subject of a joint discussion with Section G during the present meeting, so that I shall not here enlarge upon it.

With regard to the use of thermo-couples, I may remark that the practical difficulties have been successfully met. The chief difficulty is, of course, to secure that the thermo-junction attains as nearly as possible the temperature of the region in which it is immersed. As ordinary flames consist of thin shells of burning gases, on either side of which there is a very rapid fall of temperature, it is necessary to use thin wires, and to dispose them so that there is no appreciable drain of heat from the junction. By using wires of different gauge for the couples it is possible by extrapolation to arrive at a temperature for a couple of infinitely small cross-section, and it is also possible to make a correction for the superior radiating power of the couple as compared with the flame-gases. Without this last correction a maximum temperature of 1770° was obtained for the Bunsen flame by Waggener in Germany, and 1780° by White and Traver in America. Correcting for radiation, Berkenbusch found 1830° as the maximum temperature.

M. Féry, by an ingenious application of his beautiful optical pyrometer to a flame containing sodium, gives 1871° as the highest temperature of the flame of a Bunsen burner burning coal-gas.

The consideration of flame-temperatures has become of increasing importance in the arts owing to the use of the Welsbach mantle as a means of deriving light from coal-gas. The great improvements which have been made in the efficiency of atmospheric burners depend primarily on the fact that the smaller the external surface we can give

to a flame consuming gas at a fixed rate, the higher must be the average temperature; and since the emission of light from a mantle is proportional to a high power of the absolute temperature, a small increase of temperature is of great effect on luminosity.

The acetylene-oxygen flame in which a temperature of about 3500° prevails, not very different from that of the electric arc, is the hottest of the hydrocarbon flames, and finds some important practical uses.

I have already said something about the luminosity of flames so far as relates to the separation and glow of solid carbon. But there remains the more general question of the luminosity of flames containing nothing but gases. The older explanation of the emission of light from combining gases said no more than that the energy liberated during the reaction and appearing as heat raised the product to incandescence—that is to say, so increased the velocity of its molecules and the violence of their collisions that vibrations were set up whose wave-lengths lay within the limits of visible radiation. This explanation has long been questioned, and there is now, I think, a very general agreement that it will not suffice. The average temperature, in fact, prevailing in a flame, if attained in the product of combustion by the supply of heat from outside, does not suffice to make that substance luminous. We are therefore thrown back upon the conclusion that the generation of light in a flame is not a consequence, though it is an accompaniment, of the elevation of temperature. The question now is, Can we go any further? To do this we are led to consider individual molecular transactions instead of statistical averages, and the view presents itself that the combining atoms may, in losing their chemical energy, form directly systems of independent vibration where the radiation is such as to fall within the limits of visibility. If we picture such vibrating systems momentarily formed, it is easy to see that by their collision one with another they may acquire in a secondary way increased translational motion, and so lead to a state of things where the greater part of their energy is degraded in the form of heat. The high temperature of a flame would then be a consequence rather than a cause of its light.

This subject of the mechanism of luminosity, however, like so many others, has now become involved with the theory of electrons, and a chemist may be excused if he hesitates to pursue the subject further. Some years ago I called attention to the scantiness of our knowledge of the chemical changes that take place when metallic salts are used in flames for the production of spectra. Though there was general agreement that, for example, the yellow flame produced by common salt was due to the liberation and glow of metallic sodium, there was no agreement as to how the sodium was set free.

Arrhenius, pursuing the analogy which exists between the laws governing matter in the gaseous state and in the state of dilute solution, had previously been led to the view that the electrical conductivity of flames containing salt-vapours was due to ionisation of the salt throughout the volume of the flame. It appeared possible therefore that the luminosity might be ascribed likewise to the metal separated in the ionic state. Experimental investigation undertaken with a view to elicit information on this subject seemed to favour the view that the metal was reduced by chemical processes, and that it glowed in the un-ionised condition. Evidence seemed to point to the conclusion that, for example, when common salt is introduced into the flame of coal-gas the sodium chloride yields sodium by the conjoint action of steam and reducing gases; when liberation of the metal was prevented by adding a large quantity of hydrochloric acid to the flame the glow disappeared, but the conductivity was not always diminished. The fact that sodium salts, including the chloride, impart their characteristic glow to the flame of cyanogen and to other flames in which water is absent leads to some difficulty in finding a chemical explanation, and it must be admitted that a direct thermal dissociation of an alkaline halide or oxide is not out of the question. The interval of detachment of the metallic atom may be exceedingly brief, but it must be remembered that even so short a time as the interval between the molecular encounters in a gas at a high temperature is still sufficient for the emission of thousands of undisturbed characteristic vibrations. The experiments to which I have alluded have been followed up with great industry and success by Professor H. A. Wilson, who has added much to our knowledge of the electrical condition of the flames containing vaporised salts; but the question of the condition of the luminous gas is still far from being settled. Very interesting and important investigations have been carried out by Lenard, who has shown that the stream of luminous vapour produced from a sodium salt in a Bunsen flame is deflected in an electric field in such a way as to indicate that the vapour is positively charged; but he gives reason for believing that the charged condition is intermittent with the neutral condition. The lines in the spectrum of an alkali metal are divisible, as is well known, into distinct groups or series, in each of which the oscillation frequencies corresponding with the lines are in a definite mathematical relationship. The principal series, which include the lines seen individually as such in ordinary flame spectra, are, according to Lenard, due to the electrically neutral atoms. In a salted spirit flame, and in other flames of low temperature where only lines of the principal series are represented, the stream of luminous gas does not behave in an electric field as if it were charged. In the flame of coal-gas burnt in a Bunsen burner the salt-vapour gives, in addition to the distinct lines of the principal series, diffuse bands of luminosity on the dark background, which, according to Lenard, represent the undeveloped subordinate series; and it is the atoms emitting these series that are deflected in the electric field. It is inferred therefore that the light in a salted Bunsen flame comes from different groups of centres of emission—the principal series from the neutral atom, and the lines of the first, second, and third subordinate series from atoms which have lost respectively one, two, and three electrons. Lenard goes further, and shows that the salt-vapour in a Bunsen flame, as in the flame of the electric arc, emits these different kinds of radiation from different structural regions; thus the vapour at the edge of the flame is electrically neutral, and gives only the lines of a principal series.

The negative electricity in a salted flame would, according to Lenard, be disembodied, and recent experiments by Gold confirm the view that the negative carrier in flames is a free electron. In connection with this subject I ought to allude to an investigation by Tufts, which seems to throw some doubt on the conclusions which were drawn from the experiments made by Professor Wilson, Dr. Dawson, and myself; and I must also mention an important contribution to the subject recently made by Professor Hartley, in which considerable light is thrown upon the chemical changes undergone by compounds of the alkaline earth metals when they are introduced into flames, and upon the relation of these changes to the various spectral features. I am afraid, however, that it would be wearisome if I were to prolong this summary, and I must be content to leave it without doing justice to those who are engaged upon the work. The subject is obviously one of fundamental importance in relation to spectrum analysis, and my own slight connection with it has only strengthened my opinion that there is still a great deal connected with the genesis of spectra that requires the attention of the chemist even more than that of the physicist. Spectrum analysis arose under the joint influence of Bunsen and Kirchhoff, and I think its problems still call for more combined work on the part of chemist and physicist than has latterly been the custom.

Having given a short summary of the present state of knowledge on one particular chemical topic, I may perhaps be permitted to conclude my Address with a few general observations relating to the science as a whole.

The contemplation of such a life as that of Berthelot

makes us realise in a vivid way the progress of chemical science. He was a chemist without limitation, his activity extending over the whole range of the science, physical, inorganic, and organic. Whilst we must not forget his exceptional powers, we cannot help feeling how different in its extent was our science when he entered upon his labours from what it was when they ceased, and we cannot help feeling how vain it now is for anyone to hope for so imperial a sway.

Yet it is difficult to believe that the state of chemistry can ever have been more interesting than it is at the present moment, or that anyone who sighs for the good old times can do so from anything but the love of a quieter life. We need not go back more than twenty years to find a sharp contrast. At that time there was indeed no want of activity, but it was that of a band of travellers who had left their frontier adventures far behind, and were marching steadily over a wide and almost uninterrupted plain. To-day we are among the mountains, with new peaks and prospects appearing on every side. Truly a steady head is required; and well may we ask, Whither are we going and where is the path of progress and of safety? I rejoice to live in such times; but I feel no competence to describe them, still less can I pretend to have vision keen and comprehensive enough to let me figure as a guide.

One of the penalties of devotion to a progressive science is the constant feeling of being left behind, and the knowledge that, while we are attending to our personal task, things are happening, near or far, that may, for all we know, be affecting the simplest facts and the most elementary principles on which we have been accustomed to rely. This is a feeling that may well prevail at the present day. At the same time I do not think there is any occasion for panic, and I cannot help regretting the somewhat sensational language that has been used, even within our own circles, in regard to recent discoveries. The revelations attendant upon the investigation of radio-activity do indeed mark a distinct epoch in the history of chemical discovery, but that they entail anything like an unsettlement of our scientific articles of faith is not to be admitted for a moment. They make us realise in perhaps a not unprofitable way that scientific knowledge and scientific theories are necessarily proximate, never ultimate, and that ideas which may have been entertained for a long time without modification, and so have begun to seem perpetual, are, after all, only provisional.

There is certainly some embarrassment on finding that a substance like radium, which according to the conventions would be called a chemical element, breaks up so as to give substances which, according to the same conventions, are likewise called elements. But the confusion is one of terminology and not of ideas. I think it likely that few chemists of my own generation have been in the habit of regarding the conventional elements as the ultimate compositional units of matter. We know that in our own country distinguished men of science like Sir William Crookes and Sir Norman Lockyer have always insisted on the complex nature of the elements, and I suspect there are many among us who might own to having made sober, if unsuccessful, attempts at the resolution of elements before the days of radium.

The perplexities of chemists at the present day do not come, I think, from the novelty of the ideas that are being presented to them, but from the great rapidity with which the whole science is growing, from the invasion of chemistry by mathematics, and, in particular, from the sudden appearance of the subject of radio-activity with its new methods, new instruments, and especially with its accompaniment of speculative philosophy. There is an uneasy feeling that developments of great importance to the chemists are being made by experiments on quantities of matter of almost inconceivable minuteness. Spectrum analysis of course took chemistry beyond the limits of the balance, but the new materials which it disclosed could at least be accumulated in palpable quantity. With radio-activity we seem, in relation to the ponderable, almost to be creating a chemistry of phantoms, and this reduction in the amount of experimental materials, associated as it is with an exuberance of mathematical speculation of the most bewildering kind concerning the nature, or perhaps I should say the want of nature, of matter, is calculated to perturb a stolid and earthy philosopher whose business has been hitherto confined to comparatively gross quantities of materials, and to a restricted number of crude mechanical ideas. He is tempted to think of Falstaff's reckoning, and to explain with Prince Henry, "Oh, monstrous! but one halfpennyworth of bread to this intolerable deal of sack!" Experimental science has latterly been spun to greater and greater fineness, until in the region of the N-rays the objective element seems to have disappeared altogether.

I should, however, gravely abuse the position in which I am allowed to speak for the moment as a representative of chemists if I failed to express profound admiration for the masterly work which has been accomplished by the pioneers of the science of radio-activity. All that I wish to say beyond that, is in explanation of a certain awe or trepidation which chemists of the older school may feel in the presence of such bold explorers; and I am the more tempted to say something on the subject, because in recent times, before the advent of radium, a good deal has happened which has given chemists occasion to ask themselves whether chemistry was not beginning, as it were, to drift away from them.

The most conspicuous development of the science during the past twenty years has been, of course, on the physical side, and abundant have been its fruits; but it has seemed to demand from chemists habits and endowments which they did not normally possess, and which they could not easily acquire. I was much struck by a remark made to me a few years ago by a distinguished chemist, who is, I think, the most perfect manipulator I have ever seen at work, to the effect that he felt himself submerged and perishing in the great tide of physical chemistry which was rolling up into our laboratories. Now, it is precisely such men that must be preserved to chemistry. Though chemistry and physics meet and blend, there is, I believe, an essential difference between the genius of the chemist and the genius of the physicist, and I venture to think that some insistence on the primary functions of a chemist is not untimely. The chemist's first qualification is that he shall be master of a peculiar craft; his greatest merit that he is a consummate workman; his distinctive power a nicety of discrimination in questions affecting the composition and quantity of materials. He is not given to elaborate theories, and is usually averse to speculation; nor has he usually an aptitude for mathematics. Such the normal chemist is, or was, and such I hope he always may be—naked perhaps in some respects, but unashamed.

There seems to be a solicitude in some quarters to make a chemist something more than a chemist, a solicitude which, if gratified, will, I believe, make him something less than one. We are told, for example, that a chemist should be a mathematician. I do not admit it for a moment. Some mathematics he must of necessity have —that has always been admitted—but in proportion as chemistry develops on the mathematical side does it become important, not that our chemists should be trained ln mathematics, but that they should be more than ever carefully trained in the art of exact experiment; that their methods of work, their powers of observation, and, if possible, their experimental conscience, if I may use the expression, should acquire a finer edge. There is never more cause for anxiety than when we see a mathematical theory awaiting the delivery of the confirmatory facts, and there is nothing more important for chemistry than the continual recruiting of that old guard which will be ever ready to stand to arms on the appearance of an eager theorist.

I do not for a moment wish to disparage the adventurous spirits within or outside our science, still less do I wish to range myself with those who meet new ideas with

mere objurgation or raillery. We must be content to see new alliances and new activities on the frontiers that separate us from other sciences; content to see many new kinds of chemistry arise in which we cannot all effectually participate. Chemistry is becoming bewildering in its extent, and it would be a great misfortune if this led to the notion that every chemist must try to enlarge his ambit to its confines and fit himself for every variety of work. Those of us who have responsibilities as teachers cannot, I think, be too careful, lest in the attempt to secure breadth we may encourage shallowness and fail to give our students that peculiar and time-honoured discipline in exactitude of work in chemistry proper, which has characterised the chemists of the past, and which is infinitely more important than superficial dealings with a great variety of processes and appliances. I confess that I have frequent misgivings as to whether our modern courses of instruction may not tend to turn out chemists more learned in the science and less perfect in the art than was the case under the ancient *régime*. There was, after all, great virtue in the system which often detained a student day after day, or perhaps week after week, on a single problem of chemical composition such as is involved in the exact analysis of fahl-ore. It is not easy to meet all requirements, but I think we shall all agree that, whatever is left undone, we must make a chemist a good craftsman. It is of the utmost importance that those whom we send out to work in the newer fields shall take with them the resources that have proved most serviceable in the old, and I think it is by supplying such men for special service, rather than by attempting to shift the centre of gravity of the whole system of chemical education, that we can best serve the newer interests.

Another perturbation within the chemical camp in recent times has come from the region of philosophy. Even before the days of radium we have been accused of clinging too fondly to our atomic theory and of stating our knowledge too exclusively in terms of that theory. We are said to have drifted into a dogmatism as real as any we ourselves have had to attack, and to shut our eyes to the light which will enable us to orient ourselves truly in the wide realm of thought. The answer that most of us would give would be, that we value our hypotheses according to their productiveness in new knowledge, and that it is, on the whole, perhaps better to over-exalt an hypothesis that is fertile than from high considerations of philosophy to allow our ideas to become so fluid that they can afford no rigid framework for thought. I think that the attempts to view chemical phenomena apart from the atomic hypothesis, interesting as they undoubtedly are, have not made us feel that this hypothesis has either misled us in any matter of fact or obscured any pathway that we might have followed with greater profit. The value of the thermo-dynamical treatment of chemical problems is attested by its fruitfulness in promoting fresh discoveries; and here we may welcome a valuable adjunct to the atomic hypothesis. But I do not think we are called upon to acclaim a new method of treating old questions unless it promises some more tangible result than an alleged improvement of our intellectual morals.

If, as I have ventured to hint, mathematics brings with it an element of danger into chemistry, I think that the intrusion of metaphysics would give far greater cause for apprehension. Philosophy always stands with open arms desiring a closer embrace of all the sciences, of which she declares herself to be the fond mother, whilst Science, as we understand the term, has stood reluctant, suggesting, as someone has wittily remarked, that she regards Philosophy rather as a mother-in-law. It may perhaps be desirable, especially in the present state of things, that scientific men should allow themselves to become a little more interested in deep questions affecting all knowledge, and should at least examine with some care the gifts that Philosophy is so anxious to bestow upon us. I have a fear that otherwise in the elaboration of scientific theory we may find ourselves embroiled in an unequal contest with what I cannot but regard as the traditional enemy—I mean the unmitigated metaphysician—and the suggestion that I make is, to tell the truth, not so much from the hope of gain as from the desire for self-defence and the safe preservation of the methods that have served us so well in the past.

I think the accusation that we delude ourselves into the belief that our hypotheses are final truth is not true of any thoughtful chemist; the great men of science have surely possessed that quality of mind which philosophy would most approve. If, as has often been remarked, Faraday was mathematically-minded, though untrained in mathematics, it seems not less true that he stood in the same relation to philosophy. When, for example, he was asked to express his opinions on the atomic theory, he wrote as follows:—

"I do not know that I am unorthodox as respects the atomic hypothesis. I believe in matter and its atoms as freely as most people—at least I think so. As to the little solid particles, which are by some supposed to exist independent of the forces of matter, and which in different substances are imagined to have different amounts of these forces associated with, or conferred upon, them (and which even in the same substance, when in the solid, liquid, and gaseous state, are supposed to have like different proportions of these powers), as I cannot form any idea of them apart from the forces, so I neither admit nor deny them. They do not afford me the least help in my endeavour to form an idea of a particle of matter. On the contrary, they greatly embarrass me; for after taking account of all the properties of matter, and allowing in my consideration for them, then these nuclei remain on the mind, and I cannot tell what to do with them. The notion of a solid nucleus without properties is a natural figure or stepping-stone to the mind at its first entrance on the consideration of natural phenomena; but when it has become instructed, the like notion of a solid nucleus, apart from the repulsion, which gives our only notion of solidity, or the gravity, which gives our notion of weight, is to me too difficult for comprehension; and so the notion becomes to me hypothetical, and, what is more, a very clumsy hypothesis. At that point, then, I reserve my mind as I feel bound to do in hundreds of other cases in natural knowledge."

This is the attitude of mind, I think, of all thoughtful chemists; if they do not exhibit it ostentatiously it is only because it is as disturbing to the proper work of a chemist for him to be constantly dwelling on the inward nature of his hypotheses as it is distracting in ordinary life to have men always talking about their emotions.

Few, I think, will deny that the atomic theory stands to-day as an indispensable instrument for productive chemical work; it has neither had its day nor ceased to be. Physicists have never been quite satisfied with the hard invisible ball of specific substance and definite mass which has served chemistry so well. They have given it bells, have made a vortex ring of it, and have indeed done much that few chemists can understand to make it meet the exacting requirements of their science. But to us it has always been the same; what we have done to it has been external; we have given it, vaguely perhaps, a charge of electricity, a store of energy; we have attached the hooks or rods of valency, but we have not meddled with its interior. We are now called upon by chemical considerations of change of composition, as well as by other considerations more recondite, to subdivide our atom, to credit it with an unsuspected store of energy, to consider it a congeries of unsubstantial electrons. We should wish, of course, to know that the evidence is good enough, but otherwise there can be no possible objection from our side; it will undo nothing that has been done, and we may have good hopes that it will lead to the doing of many new things in chemistry. The newer theories are in consonance with the old in one most vital point; they afford those mental pictures of phenomena which most of us find indispensable for fruitful work. They do not belong to what Professor Schuster has characterised as "the evasive

school of philosophy." "Those," he says, "who believe in the possibility of a mechanical conception of the universe, and are not willing to abandon the methods which from the time of Galileo and Newton have uniformly and exclusively led to success, must look with the gravest concern on a growing school of scientific thought which rests content with equations correctly representing numerical relationships between different phenomena, even though no precise meaning can be attached to the symbols used." Most of us, I think, will take comfort in this pronouncement and rejoice that if our conception of the atom is to be transformed, it may still be represented as having some kinship with what Sir Henry Roscoe's famous examinee described as the "square blocks of wood invented by Dr. Dalton."

CORRESPONDENCE.

THE NITROGEN GROUP OF ELEMENTS.

To the Editor of the Chemical News.

SIR,—In past communications to the CHEMICAL NEWS I have drawn attention to thermo-chemical equivalence.

By grouping the elements, we find that the nitrogen group contains a similar relationship to that already shown as regards those elements we have considered individually, and that they also have a group relationship pointing to—if the theory is fully carried out—a more complete comprehension of the nature of these elements than that arrived at by the atomic theory.

The data at hand show that the oxides and chlorides at once give the necessary relations for supporting the belief in the thermo-chemical equivalents of the elements already treated. They also show that in these equivalents of similarly grouped elements, as applied at any rate to the nitrogen group, these equivalents are approximately simple multiples of one another, such as 2, 3, &c.

Finally, where apparently utter discrepancy occurs in such thermo-chemical relations, they may still be shown to point to a confirmation of the views already stated if considered dynamically.—I am, &c.,

J. C. THOMLINSON.

NOTICES OF BOOKS.

Stereochemistry. By A. W. STEWART, D.Sc. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1907.

THE author of this text-book may be congratulated upon the production of a work which students of physical chemistry will find of the utmost value. It is written in remarkably clear language, such as too often does not appear to be at the command of a writer of deep knowledge, and no mass of detail is allowed to obscure the main issues. The book is divided into two sections. The first deals with stereoisomerism, firstly when it is accompanied by optical activity, and in the second place the numerous cases of stereoisomerism without activity are discussed. The second section deals with stereochemical problems into which isomerism does not enter, and includes a full account of the most important researches connected with the phenomena of steric hindrance. The reader who is not specially interested in this branch, and who thus requires only a general knowledge of the principles involved, is advised to omit certain pages, and to read only the summaries which have been carefully written for his special benefit. The relations between space formula and chemical properties, and the effects of substitution upon stability are also considered in this part of the book; in the course of an admirable discussion of the various space formulæ, which have been proposed for the benzene molecule, the author expresses the opinion that Collie's formula is superior to all others, and that in essentials it is correct. In an appendix full directions for the construction of models to illustrate stereochemistry, and information as to where ready-made sets can be procured, are given. The value of the book lies, perhaps not so much in the vast amount of material it contains nor even the care with which this has been selected and arranged, but more particularly in the constant allusions to unsolved problems, to discrepancies, still unexplained, between facts and current theories, and to the directions in which fruitful research may be prosecuted. The admirable summaries throughout the text will do much to clear away the difficulties of the subject and to help the reader to get a firm grasp of the main principles of stereochemistry.

Peat: Its Use and Manufacture. By PHILIP R. BJÖRLING and FREDERICK T. GISSING. London: Charles Griffin and Co., Ltd. 1907.

THIS book gives a short and interesting account of the uses of peat for all purposes, special stress being laid upon its importance as fuel. As an introduction to larger works upon the subject it will be found excellent, being clearly written and well illustrated. The problem of the drying of peat by air, artificial heat, and pressure is considered at some length, and the objections to existing processes are carefully explained; tables of the ultimate analysis of peats from all parts of the world are included, and the manufacture of peat fuel by the more commonly employed processes is described and illustrated. Its uses as fuel, its special requirements in the way of fire-grates, &c., in order that it may burn satisfactorily, and its uses otherwise than as fuel form the subjects of the last two chapters, in the former of which especially much valuable information as to tests and results is contained.

Séance Solennelle de Distribution des Prix de Concours. ("Meeting for the Distribution of the Competitive Prizes"). Geneva: W. Kündig et Fils. 1907.

THIS number of the Reports of the University of Geneva contains a short biographical notice of Sir Humphry Davy, who died in Geneva in 1829, and in whose memory the Davy prize was founded by his widow. The professor of theoretical and technical chemistry at the University, Philippe A. Guye, delivered the lecture which is reprinted here, and which contains a generous appreciation of Davy's scientific work. The volume also includes a list of the students upon whom degrees were conferred in 1906, together with the reports of the Rector and Juries appointed to decide the awards of the various prizes offered by the University.

Quarterly Journal of the Institute of Commercial Research in the Tropics. Liverpool University. Vol. II., No. 4. Liverpool: The Offices of the Institute. London: Williams and Norgate. 1907.

THE fourth number of Volume II. of this journal contains outlined accounts of the various expeditions which have been dispatched by the Institute to European countries and to the United States to study the working of similar institutions, as well as to West Africa, to investigate more especially problems connected with rubber, cocoa, fibre, and maize. During these West African expeditions a large quantity of valuable botanical and entomological material was collected, and the Institute has also to chronicle important commercial results in the way of improvement of produce, effected by native farmers who have followed the instructions given by the Institute's representatives. The journal contains articles describing the

analysis of various tropical products, among which special attention must be called to the paper by the chief chemist, Dr. Spence, on the chemical nature of the resinous substances always found in crude rubber coagulated by the usual methods from latex, and upon possible means of improving inferior rubber containing a large proportion of these resinous substances. The report shows that the assistants at the Institute are devoting their energies to its service with remarkable enthusiasm, and are doing work which will be of material benefit to the development of the resources of tropical regions.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlv., No. 1, July 1, 1907.

Direct Hydrogenation of the Anhydrides of Aliphatic Acids.—Paul Sabatier and A. Mailhe.—The hydrogenation of anhydrides in presence of reduced nickel leads to a splitting of the molecule into aldehyde and acetic acid. Thus, with acetic acid anhydride the reaction is $\frac{CH_3.CO}{CH_3.CO}>O + H_2 = CH_3.CO.H + CH_3.CO.OH$. Then the greater part of the aldehyde is itself hydrogenated, giving ethyl alcohol, which is partially etherified by the vapours of acetic acid, giving water and ethyl acetate, $\frac{CH_3.CH_2}{CH_3.CO}>O$. The water thus formed transforms some of the acetic anhydride into acid. It is noteworthy that the nickel is not affected by the acetic acid generated. With other anhydrides the principal reaction is in all cases the splitting of the molecule into acid and aldehyde, the hydrogenation of which yields the corresponding alcohol. A certain amount of ether salt, $\frac{R.CO}{R.CH_2}>O$, results from the alcohol and acid formed during the reaction. The amount of ether salt decreases as the amount of carbon in the anhydride increases. Reduced copper at 200—210° acts like nickel, but is less active, and when it is used the proportion of alcohol formed, and therefore of ether salt, is much less. The copper is itself much more rapidly affected by the reaction than nickel.

Synthesis of Secondary Isoamyl Alcohol, $(CH_3)_2=CH—CH(OH)—CH_3$. — Louis Henry. — The oxide of isobutylene, $(CH_3)_2=C\overset{O}{\diagdown\diagup}CH_2$, reacts with a magnesium organic compound in the same way as its isomer, isobutyric aldehyde, and the author is inclined to think that it is converted into this isomer, or at any rate it undergoes some atomic transformation. When monochloracetone acts on two molecules of methyl-magnesium bromide the complex $\begin{matrix}CH_3\\CH_3\end{matrix}>C(O.MgBr)—CH_2Cl$ is formed. Under the influence of heat this gives Cl.MgBr and isobutylene oxide, which is converted into the secondary alcohol, $(CH_3)_2=CH—CH(OH)—CH_3$, by the further action of the methyl-magnesium bromide. The author has no doubt that ethyl monochloracetate, $ClCH_2—CO(OC_2H_5)$, with three molecules of the magnesium compound would yield secondary isoamyl alcohol, but he has not yet investigated this point. When monochloracetyl chloride, $ClCH_2—COCl$, acts on three molecules of methyl magnesium bromide a violent reaction occurs, and an appreciable quantity of secondary isoamyl alcohol is formed.

Absolute Atomic Weight of Chlorine.—G. D. Hinrichs.—If Ag = 108, Cl = 35·5, the ratio AgCl : Ag is 1·32870. The change for Ag = −30, for Cl = +93; variations for Ag = 3⅓, for Cl = 107. When the figures obtained by different investigators from Berzelius (1820) to Richards (1905) are examined, it is found that the excess in the fifth place of decimals has been reduced, by perfecting the method, from −85 to −3. Since this excess represents milligrammes in 100 grms. of silver the agreement of the later experiments with the theory of absolute atomic weights is remarkable, and the author adduces this agreement as an argument in favour of the perfect commensurability of the atomic weights of silver and chlorine.

Determination of Phosphorous Acid.—C. Marie and A. Lucas.—To determine phosphorous acid by permanganate in alkaline solution, a known volume of standard permanganate is warmed with potassium carbonate, and the phosphorous acid introduced into it. A brown precipitate of dioxide is at once formed. It is left for about fifteen minutes at 80°, and then a known volume of strongly acid solution of Mohr's salt is added. The precipitate at once dissolves, and the excess of ferrous salt is titrated by means of the solution of permanganate. It is best to determine the ratio of the two solutions (Mohr's salt and permanganate) by a blank experiment carried out under the same conditions. The strength of the permanganate can be determined by the usual methods, but it is preferable to use a substance which can be oxidised in an alkaline medium. Calcium formate is very suitable for this purpose. The equation is—

$$4KMnO_4 + 3Ca(CO_2H)_2 = 4MnO_2 + 3CaCO_3 + K_2CO_3 + 2KHCO_3 + 2H_2O.$$

Phosphites and hypophosphites which are readily oxidised to phosphites can be determined by this method.

Action of Chlorine and Sulphur Chloride on some Oxides.—F. Bourion.—When chlorine and sulphur chloride act simultaneously on zirconium oxide heated to a red heat crystals of $ZrCl_4$ are formed. These crystals retain some sulphur chloride, but may be purified by cooling them in a current of chlorine or subliming them in a current of hydrogen or dry chlorine. Glucinum oxide gives the chloride $GlCl_2$ under the same conditions, but titanium yields chiefly a yellow very volatile substance, which is a titanic oxychloride. The oxides of lanthanum, cerium, europium, gadolinium, terbium, and dysprosium all give chlorides of the type MCl_3, all of which are white, with the exception of $DyCl_3$, which is light yellow. The four last named elements yield chlorides which when fused form crystalline masses. They are only very slightly volatile at their melting-points, and give colourless solutions which are but little hydrolysed. Gadolinium and dysprosium give oxychlorides when air is passed over their fused chlorides. DyOCl is yellowish green, and GdOCl forms a white amorphous-looking mass. These oxychlorides are not volatile at a red heat; they dissolve in dilute sulphuric and nitric acid after some days.

Diglycolic Acid and its Homologues.—E. Jungfleisch and M. Godchot.—Diglycolic acid can be prepared by treating a molecule of sodium ethyl glycolate in anhydrous ether with a molecule of ethyl monochloracetate:—

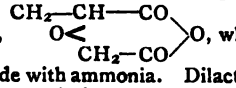
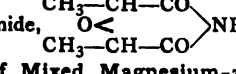
$$C_2H_5—CO_2—CH_2—Cl + ONa—CH_2—CO_2—C_2H_5 = NaCl + C_2H_5—CO_2—CH_2—O—CH_2—CO_2—C_2H_5.$$

The diglycolic ether is separated by fractional distillation and gives the acid on saponification. The diethyl ether of the new compound methyl diglycolic acid may be prepared by the action of sodium ethyl glyncolate upon ethyl α-bromopropionate sodium ethyl lactate upon ethyl chloracetate:—

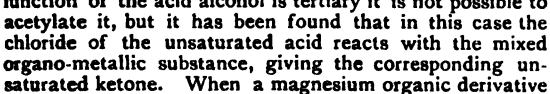
$$C_2H_5—CO_2—(CH_3)CH—Br + NaO—CH_2—CO_2—C_2H_5 = NaBr + C_2H_5—CO_2—(CH_3)CH—O—CH_2—CO_2—C_2H_5;$$

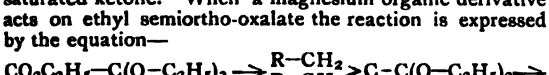
$$C_2H_5—CO_2—CH_2—Cl + NaO—CH(CH_3)—CO_2—C_2H_5 = NaCl + C_2H_5—CO_2—CH_2—O\ CH(CH_3)—CO_2—C_2H_5.$$

It is an insoluble liquid boiling at 122—125° under 20 mm. Its density at 20° is 1·0743. From it may be prepared the free acid, which is a hygroscopic substance melting at about 30°. Its alkaline and alkaline earth salts are very

soluble in water and insoluble in alcohol. When distilled *in vacuo* it gives an anhydride,  , which yields a methyl diglycolic imide with ammonia. Dilactylic ether with a concentrated aqueous solution of ammonia gives dilactylic diamide, which readily loses one molecule of ammonia, giving dilactylic imide,  .

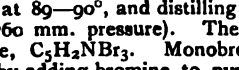
Syntheses by means of Mixed Magnesium-zinc Organic Derivatives. Unsaturated αβ - Acyclic Ketones.—E. E. Blaise and M. Maire.—Primary or secondary acid alcohols corresponding to β-chlor acids are readily transformed into acetic ethers, which, when treated with thionyl chloride, give the acid chlorides; these last react with the mixed magnesium-zinc organic derivatives, giving β-acetoxy-ketones, which may be saponified quantitatively to the unsaturated ketones. When the alcoholic function of the acid alcohol is tertiary it is not possible to acetylate it, but it has been found that in this case the chloride of the unsaturated acid reacts with the mixed organo-metallic substance, giving the corresponding unsaturated ketone. When a magnesium organic derivative acts on ethyl semiortho-oxalate the reaction is expressed by the equation—



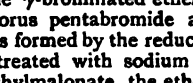


For this reaction it is necessary to employ a large excess of metallic derivative.

New Brominated Derivatives of Pyridine.—L. Barthe.—Sodium hypobromite has no action upon pyridine at temperatures below 100°, but if hydrochloric acid is added gradually to a mixture of equal volumes of pyridine and hypobromite, and the whole is heated, a golden-yellow liquid is obtained with an odour like that of nitrobenzene. When the solution is evaporated a crystalline residue is left, composed of sodium chloride and chlorate, and a brominated organic substance, which may be isolated by means of absolute alcohol, from which it separates in white crystals. The properties and analysis of these crystals show that they are pyridine bromhydrate, $C_5H_5N.HBr$. If bromine is added to the yellow liquid mentioned above, on cooling red crystals separate; they are very stable, fusing at 89—90°, and distilling without decomposition at 230° (760 mm. pressure). These crystals are tribromopyridine, $C_5H_2NBr_3$. Monobrompyridine may be prepared by adding bromine to pyridine and evaporating off the excess of the former on a water-bath. A gummy residue is thus obtained, from which may be extracted colourless crystals, by allowing it to stand with alcohol. These consist of C_5H_4NBr.

Action of γ- and δ-Brominated Ethers on Cyanacetic, Malonic, and Methyl Malonic Ethers.—G. Blanc.—When the γ-brominated ether, resulting from the action of phosphorus pentabromide and alcohol on the mixture of lactones formed by the reduction of αα-dimethylsuccinic acid, is treated with sodium ethyl cyanacetate, malonate, or methylmalonate, the ether of 2 . 2-dimethylcyclopropane carboxylic acid,  , is formed.

The isopropylcyclopropane carboxylic acid is made similarly, starting with isopropyl succinic acid, while the product of the condensation of dimethyl-3 . 3-bromovaleric acid with sodium ethyl malonate or methyl malonate is dimethyl-3 . 3-pentanoic acid (4 . 5),—



MISCELLANEOUS.

British Association for the Advancement of Science.—The following were the Officers and Committee of Section B (Chemistry) at the Leicester Meeting of the British Association:—

President—Prof. A. Smithells, B.Sc., F.R.S.

Vice-Presidents — Prof. Wyndham Dunstan, M.A., LL.D., F.R.S.; Prof. W. J. Pope, F.R.S.; Sir William Crookes, F.R.S.; Sir Henry E. Roscoe, F.R.S.

Secretaries — Prof. A. W. Crossley, D.Sc., Ph.D., F.R.S. (Recorder); E. F. Armstrong, Ph.D., D.Sc.; F. M. Perkin, Ph.D.; J. H. Hawthorn, M.A.

Committee—Prof. R. Abegg; Prof. H. E. Armstrong, F.R.S.; J. L. Baker; J. Carter Bell; Prof. Phillips Bedson; Dr. O. Boudouard; Dr. Horace T. Brown, F.R.S.; Dr. Cain; Dr. F. D. Chattaway, F.R.S.; Sir James Dewar, F.R.S.; Dr. Desch; Prof. H. B. Dixon, F.R.S.; Prof. Divers, F.R.S.; Prof. Donnan; T. Fairlie; Prof. F. Haber; A. Vernon Harcourt, F.R.S.; A. D. Hall; Prof. G. G. Henderson; H. Hilton; Dr. H. R. Le Sueur; Dr. T. M. Lowry; Dr. F. M. Jaeger; Dr. H. O. Jones, Prof. Kauffmann; Dr. A. Mackenzie; Dr. H. Marshall, F.R.S.; Prof. McLeod, F.R.S.; Prof. H. A. Miers, F.R.S.; Dr. Forster Morley; Prof. R. Nasini; Dr. R. H. Pickard; Prof. Orton; H. Ramage; Sir William Ramsay, K.C.B., F.R.S.; Prof. T. W. Richards; Prof. J. Sakurai; Prof. Tilden, F.R.S.; Prof. Senier; Dr. Ida Smedley; Prof. Soddy; Dr. J. F. Thorpe; Prof. A. Tschitschibabin; Dr. A. E. Tutton, F.R.S.; W. Marshall Watts; Prof. A. Werner.

The Papers brought before the Section were as follows:—

President's Address.

Discussion on "Valency," opened by Prof. W. J. POPE, and in which Prof. Werner (Zürich), Prof. Abegg (Breslau), Prof. Jaeger (Amsterdam), Prof. Kauffmann (Stuttgart), Prof. J. J. Thomson, Mr. W. Barlow, and others took part.

Joint Discussion with Section G (Engineering) on "Explosion Temperatures," opened by Mr. DUGALD CLERK, and in which Dr. Boudouard (Paris), Prof. Haber (Karlsruhe), Prof. B. Hopkinson, Prof. H. B. Dickson, and others took part.

Prof. PHILLIPS BEDSON—Experiments illustrative of the Inflammability of Mixtures of Coal-dust and Air.

Prof. H. B. DIXON—Ignition-point of Gases.

Prof. H. E. ARMSTRONG—Condition of Salts in Concentrated Solution.

Prof. Sir JAMES DEWAR and Dr. H. O. JONES—Carbonyl Compounds.

Dr. K. S. CALDWELL—Conductivity of Electrolytes in Pyridine and other Solvents.

Dr. A. MCKENZIE—Application of Grignard's Reaction.

Prof. TSCHITSCHIBABIN (Moscow)—Triphenylmethyl.

Prof. JAEGER—On Substances which form three different Liquid Phases.

Dr. CHATTAWAY—Copper Mirrors.

Prof. RICHARDS—Atomic Weights.

Dr. BOUDOUARD—Carbon Suboxide.

Mr. A. E. PRATT—Calcium; its Properties and Possibilities.

Reports of Committees—

The Transformation of Aromatic Nitramines.

The Study of Hydroaromatic Compounds.

Preparation of a New Series of Wave-length Tables of the Spectra of the Elements.

Dynamic Isomerism.

The Study of Isomorphous Sulphonic Derivatives of Benzene.

Discussion on "The Chemistry of Wheat and Flour, with Special Reference to Strength," opened by Mr. A. E. HUMPHRIES, President of the National Association of British and Irish Millers. The following Members

took part :—Messrs. R. H. Biffen, T. B. Wood, A. D. Hall, Horace Brown, J. L. Baker, A. J. Banks, E. F. Armstrong, E. S. Watkins.

Dr. A. D. HALL—Production of Acid or Alkaline Reactions in the Soil by Artificial Manures.

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WINTER COURSES.

Zoology, Elementary, 9 a.m.; and Zoological Laboratory, Elementary, 11 a.m. or 3 p.m.—Professor GRAHAM KERR, M.A.

Chemistry, 10 a.m.; and Chemical Laboratory, 10 a.m. to 4 p.m.—Professor FERGUSON, M.A., LL.D., F.S.A.

Organic Chemistry, Elementary.—T. S. PATTERSON, Ph.D.

Anatomy, Junior, 11 a.m.; Senior, 1 p.m.; and Practical Anatomy, 9 a.m. to 4.45 p.m.—Professor CLELAND, M.D., LL.D., D.Sc., F.R.S., and Demonstrators.

Physiology, 12 noon; and Physiological Laboratory.—Professor NOEL PATON, B.Sc., M.D., and Assistants.

Physiological Chemistry.—E. P. CATHCART, M.D.

Materia Medica and Therapeutics, 11 a.m.; and Pharmaceutical Laboratory.—Professor STOCKMAN, M.D.

Pathology, Systematic, 3 p.m.—Professor MUIR, M.A., M.D.

Surgery, 12 noon.—Prof. Sir WILLIAM MACEWEN, M.D., LL.D., F.R.S

Midwifery, 2 p.m.—Professor MURDOCH CAMERON, M.D.

Practice of Medicine, 11 a.m.—Prof. Sir T. M'CALL ANDERSON, M.D

Clinical Medicine, 9 a.m.—Professor GEMMELL, M.D., and Professor Sir T. M'CALL ANDERSON, M.D.

Clinical Surgery, 9.15 a.m.—Professor Sir HECTOR C. CAMERON, M.D., and Professor Sir WILLIAM MACEWEN, M.D., LL.D., F.R.S.

Public Health, 12 noon, four days weekly; Public Health Laboratory, 10 a.m. to 4 p.m.—Professor GLAISTER, M.D., D.P.H. (Camb.).

Ear, 4 p.m., Mon. (University); Practical Instruction as may be arranged THOMAS BARR, M.D.

Throat and Nose, 4 p.m., Thurs. (University); Tues. or Fri. (Western Infirmary). JAMES WALKER DOWNIE, M.B.

SUMMER COURSES.

Commencing on WEDNESDAY, 22nd APRIL, 1908.

Physics, 11 a.m.—GEORGE W. WALKER, M.A.

Practical Physics, 9 to 11 a.m., or 1 to 3 p.m.—Professor GRAY, M.A., LL.D., F.R.S.

Botany, 8 a.m.; and Botanical Laboratory, 9 a.m. to 4 p.m.—Professor BOWER, Sc.D., F.R.S.

Clinical Medicine, 9 a.m.—Professor GEMMELL, M.D., and Professor Sir T. M'CALL ANDERSON, M.D.

Clinical Surgery, 9.15 a.m.—Professor Sir HECTOR C. CAMERON, M.D., and Professor Sir WILLIAM MACEWEN, M.D., LL.D., F.R.S.

Chemical Laboratory, 10 a.m. to 4 p.m.—Professor FERGUSON, M.A., LL.D., F.S.A.

Organic Chemistry, Elementary.—T. S. PATTERSON, Ph.D.

Practical Anatomy, 9 a.m. to 4 p.m.—Professor CLELAND, M.D., LL.D., D.Sc., F.R.S., and Demonstrators.

Embryology, 11 a.m.; and Embryological Laboratory, 9 a.m. to 4 p.m.—JAMES F. GEMMILL, M.A., M.D.

Applied Anatomy, 1 p.m., Mon., Wed., Fri.—ROBERT KENNEDY, M.A., D.Sc., M.D.

Practical Pharmacy, 12 noon.—Professor STOCKMAN, M.D.

Practical Physiology, 9 to 11 a.m.; and Physiological Laboratory.—Professor NOEL PATON, B.Sc., M.D., and Assistants.

Medical Jurisprudence and Public Health, 11 a.m.; and Public Health Laboratory.—Professor GLAISTER, M.D., D.P.H. (Camb.).

Practical Pathology, 1 to 3 p.m.—Professor MUIR, M.A., M.D.

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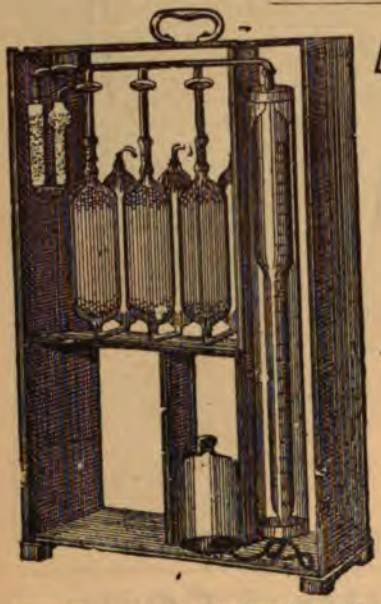

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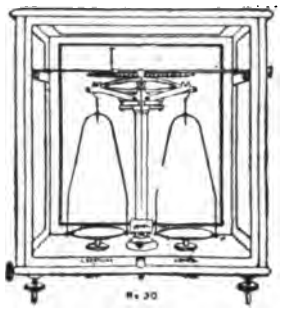

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THE CHEMICAL NEWS.

Vol. XCVI., No. 2490.

FIRST DECAY PRODUCTS OF ACTINIUM (EMANIUM).

A New Emanation, and the Formation of Helium from Actinium.

By F. GIESEL.

I. *Radio-actinium.*

In earlier articles (*Berichte*, 1904, xxxvii., 1697; 1905, xxxviii., 778) I have already stated that the artificial barium sulphate precipitates obtained from emanium solutions retain their activity for many months. Also, I noticed that the strontium sulphate separated from emanium preparations decays equally slowly (*Berichte*, 1904, xxxvii., 3966). Hence, it must be assumed that the chief constituent of these sulphuric acid precipitates is not actinium X with a half decay period of ten days, but a substance with a longer duration of life.

Recent determinations of the times of decay (period of decay to the half value nineteen days) agree very well with radio-actinium, which was, meanwhile, discovered by Hahn (period of decay to the half value nineteen and a-half days) (*Berichte*, 1906, xxxix., 1605).

From my earlier articles mentioned above, it now appeared that sulphuric acid is capable of precipitating radio-actinium, at least if strontium or barium is present. It has also already been stated (*Berichte*, 1904, xxxvii., 3965) that the insoluble sulphate can be converted into soluble chloride, and the active substance (*i.e.*, the radio-actinium) again quantitatively precipitated as carbonate (*Berichte*, 1904, xxxvii., 3965). Ammonia, on the contrary, does not precipitate it, or the radio-actinium can be carried down on precipitating the hydroxides only in presence of certain salts, *e.g.*, thorium or iron salts. Hence, probably radio-actinium belongs to the alkaline earths, or is closely allied to them. Spectrograms of the spark light of strong preparations obtained from the chloride, however, always gave only strontium as the chief constituent besides very little calcium and barium. No new lines could be detected.

Hahn used finely divided sulphur, which had been separated from sodium thiosulphate, to precipitate the radio-actinium. Similarly, I have often observed that sulphur, which separates when sulphuretted hydrogen is led into cerium or iron salts, produces the same effect. But possibly in both reactions it is not the mechanical action of the sulphur which is the cause of this, as has been assumed, but the formation of some sulphuric acid, which then undoubtedly effects the precipitation of the radio-actinium. (Sodium thiosulphate itself mostly contains some sulphate). The same holds good for the method used by Debierne and Marckwald to separate thorium (or radio-actinium) by sodium thiosulphate, when it is known that the thiosulphate is decomposed. Marckwald has already stated (*Berichte*, 1905, xxxviii., 2264) that in this method all the actinium remains in the solution, and that the thorium again slowly loses its activity. I have several times convinced myself of the correctness of Marckwald's statements. Debierne says that actinium is allied to thorium, but this must now be corrected. Actinium is never precipitated with thorium from a mixture of the rare earths of pitchblende, but always remains with the cerium earths, especially with lanthanum, as I have found.

I must mention thal I did not get my strong radio-actinium preparations free from β-radiation, and they contained some emanation, which is easily explained, for after a short time the further decay products must result. Hahn also states that the α-radiation of radio-actinium is approximately pure only a short time after its preparation.

II. *Actinium* X.

As may be inferred from what has been said above, actinium X remains practically unprecipitated by sulphuric acid. It can easily be separated from actinium by ammonia, by the well known method. But the solubility in ammonia is limited, so that the actinium X, after sufficient concentration is partially precipitated by ammonia (*cf. Berichte*, 1905, xxxviii., 778); also by alkali carbonates, in this case with traces of strontium. In the filtrate a considerable amount of actinium X still remains. All three partial separation methods applied in succession gave, on an approximate determination based on only three observations, a half constant of eight or nine days.

My statements in the *Berichte* (1905, xxxviii., 777), that actinium X is precipitated by sulphuric acid, thus require modification now that radio-actinium is known. This latter is first precipitated, and then actinium X results from it.

Sulphuric acid can be used to separate radio-actinium and actinium X.

III. *New Emanation.*

In order to test Boltwood's statement, that "actinium slowly forms radium," 0·2 grm. of a very strong emanium preparation from radium mother-liquor (*Berichte*, 1903, xxxvi., 343), which was four years old, was dissolved in hydrochloric acid, and some sulphuric acid was added after filtration. If radium had been formed, it must have been found in the precipitate which resulted. Unfortunately, this precipitate was so small that a spectrographic examination was impossible. The activity of the small filter with the substance was, however, so great that only a very small fraction of it could be used to determine the change of activity with time, and an electroscope with a very high capacity was employed. But the activity did not increase as is the case with radium, but decreased at the rate which is characteristic for radio-actinium, as was to be expected. However, small amounts of radium could not have been detected thus.

As, in consequence of the great differences in the rates of decay of radium and actinium emanations (period of decay to the half value for radium emanation four days, for actinium emanation four seconds), it is easy to detect traces of the former in the latter, the emanation of the little filter was collected during a period of some days; it was led into a test-tube closed with wadding and connected with a glass flask of about a quarter of a litre capacity. If an emanation with a longer duration of life, such as actinium emanation, were formed, it would diffuse into the glass flask. After about half-an-hour after separating the tube with the filter, the gaseous contents of the flask were introduced by displacement with water into Elster and Geitel's leakage apparatus previously partially exhausted, putting in between a securely closed wadding filter. In all experiments which were repeatedly carried out with different preparations and even with a matured actinium preparation itself, the electroscope showed the presence of an emanation by a loss of charge of 200 to 400 volts in an hour, according to the quantity and the time the radio-active substance was left in the collecting apparatus. But the emanation could not be radium emanation, for the characteristic rise of leakage value did not occur during the first one or two hours, nor the following decrease. On the contrary, a much slower increase occurred, reaching about double the original value in the first two or three days (500 to 700 volts per hour). Then the activity remained constant at this value during a time of observation of from two to three weeks. After exposing the apparatus to the air in a few hours the leakage value had sunk almost to the normal, and on the next day it reached the normal. Hence, no solid active substance (induced activity) can have been precipitated on the interior of the apparatus. No substance in the form of

dust could be present because wadding filters were used. More probably a gaseous substance, possessing an exceedingly long life, was present.

The new emanation seems to proceed from the decay of actinium emanation in minute quantities, unless an unknown substance, which in its turn gives the new emanation, is contained in the radio-actinium or emanium preparation.

IV. *Formation of Helium from Actinium.*

Almost at the same time as I prepared my radium-helium tubes (*Berichte*, 1905, xxxviii., 2299), *i.e.*, more than two years ago, I enclosed similarly 0·5 grm. of a relatively strong emanium preparation in the form of oxide in a Geissler tube, and exhausted as far as possible. The vacuum was maintained unaltered during this time, and helium could not be detected when the gas was faintly luminous. But latterly it has been possible, after heating the substance, to identify in the spectrum of the gas the D_3 line of helium. This agrees with an earlier statement of Debierne (*Comptes Rendus*, 1905, cxli., 383), who found helium in the gases developed from actinium, just as Ramsay detected it in the gases obtained from radium. —*Berichte*, 1907, xl., 3011.

THE RADIATION OF THORIUM PRODUCTS.

By OTTO HAHN.

In a recent communication on "A New Intermediate Product from Thorium (*Berichte*, 1907, xl., 1462) I reported briefly on experiments which showed that thorium does not decay directly to radio-thorium, and that probably another product exists between these two, which unlike radio-thorium emits no α-rays, but is superior to the latter in its duration of life. I gave about two years as the decay constant of radio-thorium (see Note), and estimated that the constant for this new element was seven years. (The value seven years was evidently too high).

(Note.—Shortly before my communication an article by G. A. Blanc appeared in *Lincei Rend.*, 1907, xvi., 261) on "The Decay Constant of Radio-thorium"; he found the value 737 days. Unfortunately, when I wanted to refer to this article I could not get access to it).

Further experiments have now completely confirmed the existence of this intermediate product, so that in the future I shall allude to it by the name mesothorium. In the article quoted I stated that in the technical preparation of thorium nitrate the mesothorium was separated from the thorium, but not the radio-thorium. Then there followed a decrease of the activity because the radio-thorium decayed. After some years the lowest stage was reached, and then the activity again slowly increased, as with the reformed mesothorium some new radio-thorium also resulted.

When exact measurements were taken of these processes different results were obtained for the activity according as the α-radiation, the emanation, or the β-rays were compared.

Hence, it must be concluded that besides radio-thorium and its derivatives the first members of the thorium series also emit rays, and this conclusion can be confirmed partly by an indirect and partly by a direct method.

As regards the α-rays it was formerly assumed that there were four different sorts in the thorium products. Before the separation of the radio-thorium these were distributed among thorium, thorium X, the emanation, and thorium B. Then I showed that radio-thorium emits α-rays, and hence inferred that thorium itself sends out no rays; for the 25 per cent α-activity, which Rutherford and Soddy investigated, and which is inseparable from thorium, is obviously due to the radio-thorium.

The communications on the subject of inactive thorium which have been published by various investigators can be satisfactorily explained if it is assumed that in the products examined, if they really were thoriun, by some means the radio-thorium had been separated.

I then found a fifth α-radiation product in the active precipitate of thorium, for it appeared that the substance known as thorium B has a complex nature, and emits two sorts of α-rays. The carriers of these rays were called thorium B and thorium C.

I have now come to the conclusion that a sixth sort of α-rays exists, thorium itself, and not only the radio-thorium emitting α-particles.

Although the proof of this was arrived at indirectly, nevertheless three different methods led to the same result.

The methods used were:—

1. Comparison of the activities of thorium preparations of different ages by the effect of the α-rays and of the emanation.

The differences in the effect of the emanation are greater than those of the α-rays, as the activity of thorium itself is added as a constant quantity to the measurements of the α-rays, but not to those of the emanation.

2. Preparation of thorium preparations of different age from thorium X.

The inseparable α-activity is composed of two quantities, the constant activity of the true thorium and the activity of the radio-thorium. If the latter is present with its decay products in excess, as is the case with new thorium preparations, a larger fraction of the total quantity is removed in the separation of the thorium X than in old preparations, in which less radio-thorium + thorium X is present.

3. Preparation of radio-thorium free from thorium X.

The inseparable α-activity is smaller than in any ordinary thorium preparation, as the activity of the true thorium is removed.

The existence of a typical α-radiation of true thorium seems thus proved, and the question of the so-called active thorium appears to be finally settled.

It has hitherto been assumed that the β-radiation of thorium arises only from the active deposit. Exact experiments on the origin of the β-rays were described by Levin (*Phys. Zeit.*, vii., 513). He was able to reduce the β-activity of thorium to a small percentage of its original value by separating the thorium X from the thorium or radio-thorium. Levin therefore came to the conclusion that neither thorium nor radio-thorium emits penetrating β-rays, and that such β-rays are only sent out by the last products, thorium B or C.

Recently, v. Lerch (*Phys. Zeit.*, vii., 913) has shown that thorium A also emits a kind of β-radiation, which, however, cannot be compared as regards penetrative power with that of thorium B + C. The rays are scarcely more penetrating than α-rays, and probably they are a sort of specially slow β-rays, or so-called δ-rays.

In my experiments with thorium preparations of different ages I obtained the singular result that the β-radiation of the old preparations did not differ from that of the new by the amount that was to be expected. Thus, as the thorium B and C is always proportional to the amount of emanation—under the same conditions—the fluctuations in the β-activity must follow those of the emanation effect provided that thorium B + C is the only cause of the β-rays in thorium. As the experiments did not confirm this there must be another source of β-rays in old thorium preparations.

The next thing to be done was to search for the cause of such β-radiation in the newly discovered mesothorium, and it was found that mesothorium emits β-rays. (It must be assumed that mesothorium also emits γ-rays, but this has not yet been investigated). The experiments of Levin quoted above were not affected by this, for his thorium preparations evidently did not contain mesothorium, for they were not old enough. Moreover, this small quantity was not sufficient for measurement, which, of course, was not recognised as mesothorium was not then known.

It could also be proved directly that mesothorium emits β-rays. I succeeded in separating mesothorium from old thorium preparations, which showed itself by the continual increase of activity and power of emanation. The preparations thus obtained show a β effect which is much

greater than that of equally strong radio-thorium or ordinary thorium preparations under the same conditions of emanation. I have recently obtained a preparation which emits about one hundred times more β-rays than would correspond to its α-activity. Hence, it appears that the specimen will increase considerably in α effect until the newly formed radio-thorium is in radio-active equilibrium with the mesothorium.

I hope shortly to be able to give a full statement of the numerical results elsewhere, and will here append only a list of the different thorium products with the rays they emit in order of formation.

Thorium	α rays
Mesothorium	β ,,
Radio-thorium	α ,,
Thorium X	α ,,
Emanation	α ,,
Thorium A	slow β ,,
Thorium B, Thorium C	α, $\beta+\gamma$,,

—*Berichte*, 1907, xl., 3304.

IRON CARBONYLS.*

By Sir JAMES DEWAR, M.A., D.Sc., F.R.S.,
and
H. O JONES, M.A., D.Sc.

IRON pentacarbonyl, $Fe(CO)_5$, is a yellow liquid which resembles nickel tetracarbonyl in its chemical and physical properties, but it is more stable towards chemical reagents. When decomposed by reagents it always gives rise to *ferrous* salts.

The most striking difference observed between its behaviour and that of nickel carbonyl is due to the action of light, iron pentacarbonyl being decomposed with evolution of carbon monoxide and formation of an orange crystalline solid, *diferro-nonacarbonyl*, $Fe_2(CO)_9$. This change is supposed to take place in two stages, represented by $Fe(CO)_5 = Fe(CO)_4 + CO$ and $Fe(CO)_4 + Fe(CO)_5 = Fe_2(CO)_9$, since when iron pentacarbonyl is dissolved in nickel carbonyl it is not affected by light, due, it is suggested, to the formation of an unstable compound, $FeNi(CO)_9$.

The decomposition induced by light is reversed slowly in the dark. Above 56° C. light has no action on iron pentacarbonyl; this is explained by supposing that the direct action induced by light is a change that is almost unaffected by temperature, like the reaction between ferric chloride and oxalic acid and some other photochemical actions, whereas the reverse action of carbon monoxide and the diferro-nonacarbonyl has a normal temperature coefficient.

When diferro-nonacarbonyl is heated alone a dark green liquid is produced; this consists chiefly of iron pentacarbonyl; on continued heating the green colour disappears, and iron is deposited; the change is then represented by the equation $2Fe_2(CO)_9 = 3Fe(CO)_5 + Fe + CO$.

When substances like hydrocarbons or ether are present in excess and the temperature is not allowed to exceed 100° C. an intensely green-coloured solution is obtained; no solid is deposited, and no gas is evolved. The dark green solution under suitable conditions deposits dark green lustrous crystals which represent a third compound of iron and carbon monoxide, *iron tetracarbonyl*, $Fe(CO)_4$, which has a high molecular weight. When alcohol or pyridine is used as solvent in which to heat the diferro-nonacarbonyl the solution obtained is red, and no solid could be obtained from these solutions.

Iron tetracarbonyl is very stable towards reagents; it dissolves in most organic solvents to give dark green solutions which exhibit a characteristic absorption band in the yellow. In pyridine and alcohol, however, the colour of the solution is green at first, but changes slowly on standing and quickly on warming to a deep red; the red solutions show no selective absorption.

Both diferro-nonacarbonyl and iron tetracarbonyl when decomposed by reagents such as concentrated sulphuric acid give carbon monoxide and *ferrous* salts.

* A Paper read before the British Association (Section B), Leicester Meeting, 1907.

ON THE CONDUCTIVITY OF ELECTROLYTES IN PYRIDINE AND OTHER SOLVENTS.*

By KENNETH SOMERVILLE CALDWELL.

I. *Comparison of Acids and Pseudo-acids in Pyridine.*

ALTHOUGH previous experimenters have compared acids and pseudo-acids as regards their conductivities in solvents which form hydrogen ions (*e.g.*, alcohols and mixtures of alcohols and water) (Hantzsch and Voegelen, *Ber.*, xxxv., 1001), no investigations have been carried out in solvents which are of such a nature that the acid is dissolved either entirely or partly in the form of a salt. Liquid ammonia would at once suggest itself as a suitable medium, more especially as a number of widely differing compounds have already been examined in this solvent (Franklin and Kraus, *Am. Chem. Journ.*, xxiii., 277; xxvii., 196), but owing to the obvious experimental difficulties it was not employed. The attempt to substitute the saturated amine piperidine instead of ammonia yielded results of little interest, owing to the extremely small conductivity of solutions in this solvent. The unsaturated amine pyridine, on the other hand, proved to be more suitable.

Members of the following classes of compounds were examined:—

A. Acids which exist in one form only.
   1. The strong mineral acids and sulphonic acids.
   2. Organic acids.

B. Acids which exist in isomeric forms—pseudo-acids.
   1. Nitro-compounds—(*a*) nitrohydrocarbons; (*b*) nitrophenols; (*c*) nitramines.
   2. Oximido-compounds—(*a*) oximido-carboxylic esters; (*b*) oximido-ketones and quinonoximes; (*c*) nitrolic acids.
   3. Compounds containing the group —CO.NH—.
   4. Related nitrogen compounds, *e.g.*, aminotetrazol, phenyloxytriazol carboxylicester.
   5. Ketonic-enolic compounds.
   6. Oxyazobenzenes.

The pyridonium halides in pyridine exhibit the same differences in conducting power that is noticed in solutions of their alkali salts in pyridine (Laszynski and Gorski, *Zeit. fur Elektrochem.*, iv., 290), methyl alcohol (Carrara, *Jahrb. für Elektrochem.*, iii., 12), and liquid sulphur dioxide (Walden and Centnerszwer, *Zeit. für Elektrochem.*, xi., 249); only in pyridene the difference is much more marked (*e.g.*, HCl. $\mu_{32} = 1{\cdot}16$, HBr. $\mu_{32} = 7{\cdot}12$, HI. $\mu_{32} = 27{\cdot}4$). With this exception, the "true" acids compared among themselves follow approximately the same order in pyridine as in water; a fact which also applies to the pseudo-acids. The stronger the tendency to pass into an isomeric form, *i.e.*, the more completely the pseudo-acid form is isomerised and ionised in aqueous solution, the better does its pyridine solution conduct. There is to a certain extent a parallel between the affinity constants in aqueous solution and the conductivities in pyridine. When, however, the true acids are compared with the pseudo-acids, it is noticed that in pyridine the latter yield very much better conducting solutions than do "true" acids, having approximately the same, or even very much greater, affinity con-

* Report of work carried out in Leipzig under the direction of Professor A. Hantzsch. Read before the British Association (Section B), Leicester Meeting, 1907.

stants. We may conclude that *when a hydrogen compound yields a pyridine solution of far better conducting power than is given by a true acid which in aqueous solution is dissociated to approximately the same extent as the hydrogen compound, the latter is a pseudo-acid.* Hexanitrodiphenylamine, for example, must be regarded as a pseudo-acid; for although, owing to its insolubility in water, its affinity constant has not been determined, the conductivity of its pyridine solution is far greater than that of all true acids, even the strongest mineral acids.

II. *On the Influence of Temperature on the Conductivity of Electrolytes.*

1. The influence of temperature on the conductivity of electrolytes may be expressed by the general equation—

$$\frac{d\mu}{dt} = c\left(i \cdot \frac{dv}{dt} + v \cdot \frac{di}{dt}\right);$$

where i = concentration of the ions, v = mean rate of migration of positive and negative ions, t = temperature, and c = constant.

If the effect of change of temperature on the rate of migration is the reverse of that on the degree of dissociation, a maximum in the temperature-conductivity curve is to be expected.

2. It may be deduced that, for a given electrolyte, the smaller the dielectric constant of the solvent the lower must lie the temperature of maximum conductivity.

3. These deductions are confirmed by the results of previous experiments on solutions in water (Noyes and Coolidge, *Zeit. Phys. Chem.*, xlvi., 323), methyl and ethyl alcohols (Kraus, *Phys. Review*, xviii., 40), ammonia (*Am. Chem. Journ.*, xxiv., 83), and sulphur dioxide (Walden and Centnerszwer, *Zeit. Phys. Chem.*, xxxix., 513), and especially by the results of the present investigation on solutions in pyridine. The influence of temperature on the electric conductivity of solutions in pyridine has been determined for a number of acids and pseudo-acids as well as for silver nitrate. The temperature of maximum conductivity is well marked, and the curves have been followed up to and beyond this point.

4. The curves are represented closely by the parabolic equations $\mu_t = \mu_0(1 + bt + ct^2)$, and the theoretically deduced expression $a = \frac{\mu_t - \mu_\tau}{\mu_\tau(t-\tau)^2}$ is taken as a measure of the temperature effect.

5. The observation of Walden and Centnerszwer, that for solutions in liquid sulphur dioxide the temperature of maximum conductivity is higher the greater the conductivity, has not been confirmed for solutions in pyridine.

6. The comparatively rapid decrease in the degree of dissociation with increase in temperature may partly explain the fact that numerous substances which at ordinary temperatures yield good conducting pyridine solutions appear, according to boiling-point determinations, to be undissociated.

III. *Abnormally High Values of Ionic Conductivity* (*cf.* Danneel, *Zeit. Elektrochem.*, xi., 249).

Solutions of salts which contain either the same cation or the same anion as the solvent itself (pyridonium salts in pyridine, formates in formic acid, acetates in acetic acid, and probably bromides in hydrobromic acid, and sulphates in sulphuric acid) show in these solvents an abnormally high conductivity in comparison with all other salts. Since all salts are dissociated to approximately the same extent, the abnormally high values of the conductivity of the first-class can only be explained by assuming an abnormally high value for the rate of migration of those ions which the salt has in common with the solvent.

This abnormal value of the rate of migration is, however, only an apparent one. The ions of such salts react with the solvent with exchange of a labile hydrogen atom.

AN AUTOMATIC VACUUM REGULATOR.

By A. E. ANDREWS.

In employing a vacuum pump in order to conduct an operation at reduced pressure, difficulties often arise owing to fluctuations in the degree of exhaustion obtained. This is especially the case when distilling under reduced pressure, for it often happens that the liquid either boils too violently or not at all. I found that this difficulty could be obviated by employing an apparatus constructed as shown in Fig. 1. It works automatically, and after adjustment maintains any desired pressure constant within very narrow limits.

The apparatus consists of a glass tube furnished with a side-arm (B), and having at its lower end a small aperture (A) closed by a hemispherical piece of indiarubber held in a short glass tube (V) perforated at the side and open at the top. This valve is pressed down by a spring (S), which is

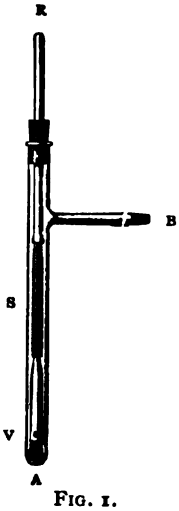


Fig. 1.

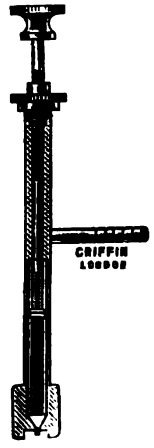


Fig. 2.

kept in position by an adjustable rod (R). The side-arm B is connected with the apparatus undergoing exhaustion. The valve is kept closed by the combined pressure of the spring and of the air in the apparatus. As the air is pumped out the pressure on the valve diminishes, until a point is reached when the external pressure is able to lift the valve, and the air thus admitted keeps the internal pressure constant. If the pressure as shown by the pump-gauge is greater than that desired, the rod R is pressed down, thus increasing the pressure of the spring, and the valve will only open when a higher degree of exhaustion is reached. By moving the rod R up or down the desired pressure may readily be obtained.

The apparatus has been constructed by Messrs. John J. Griffin and Sons, Ltd., who also make it in a form entirely of metal, in which case the sliding rod R is replaced by a screw-down rod, as shown in Fig. 2. The metal regulator seems likely to prove applicable to manufacturing plant, such as vacuum pans.

British Association for the Advancement of Science.—Mr. Francis Darwin, F.R.S., has been elected President of the Association for the year 1908-09. The meeting will be held in Dublin, from September 2nd to 9th, 1908.

Lawes Agricultural Trust.—The following gentlemen have recently been appointed on the Staff of the Rothamsted Experimental Station:—Dr. E. J. Russell, lately of the South-Eastern Agricultural College, Wye, as the Goldsmiths' Company's Assistant for the Investigation of Soils, and Dr. B. B. Hutchinson, of the Midland Agricultural and Dairy College, Kingston, Derby, as Bacteriologist.

NOTE ON THE INTERACTION OF ETHYL BROMIDE AND SILVER CHROMATE.

By ARTHUR JAQUES, B.Sc.

In presence of water, ethyl bromide and silver chromate (prepared by precipitating silver nitrate with potassium chromate—O. Mayer, *Berichte*, xxxvi., 1740) interact, yielding a red solution containing alcohol, chromium trioxide, &c., while the silver chromate is replaced by white silver bromide.

In absence of water, the reaction is slow. The two substances were placed together in a stoppered tube. In three weeks, white specks of silver bromide could be seen, and a reddish brown powder which easily went into suspension in the liquid had appeared. The volume of ethyl bromide had diminished.

The solids were filtered off, the ethyl bromide was allowed to evaporate, and aqueous potassium cyanide was poured through the filter in order to remove silver salts. The remaining solid was dried in the desiccator, but was found to be slightly changed in colour.

When heated it decomposed with evolution of light and heat, yielding chromic oxide, carbon dioxide, water, and other vapours. On treatment with aqueous caustic soda, it gave a yellow solution containing alcohol and sodium chromate. These bodies were identified by means of the iodoform reaction and precipitation with barium acetate in acetic acid solution respectively. Thus the substance is probably ethyl chromate.

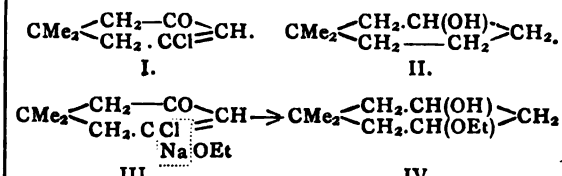
The residue obtained on heating the body always contained a small quantity of silver. Prolonged washing with potassium cyanide caused decomposition. Thus the body has never been obtained in a state of purity.

Attempts were made to wash the body with alcoholic lithium cyanide, but most of it went into the solution, from which, however, a reddish powder afterwards separated. At this point the work was suspended (1905), and it has not yet been resumed. It is hoped to obtain the substance by this method in a condition suitable for analysis at some future time.

THE

STUDY OF HYDRO-AROMATIC SUBSTANCES.*

1. *The Action of Reducing Agents on* 5-*Chloro*-3-*keto*-1 : 1-*dimethyl*-Δ^4-*tetrahydrobenzene* (Crossley and Renouf, *Journ. Chem. Soc.*, 1907, xci., 63).—Some little time since (*J. Chem. Soc.*, 1905, lxxxvii., 1487), it was shown that the principal product obtained by the action of sodium in moist ethereal solution on chloroketodimethyltetrahydrobenzene (I.) was 3-hydroxy-1 : 1-dimethylhexahydrobenzene (II.), which may be described as the limit-reduction product of the chloroketone. A further study of the reaction has proved that the addition of a small quantity of alcohol to the ether has a beneficial effect, considerably increasing the yield of hydroxydimethylhexahydrobenzene, and rendering it much easier to remove the chlorine completely from the chloroketone. As alcohol had such a decided influence, it was thought advisable to try the reduction with sodium in absolute alcoholic solution. The reaction proceeded, however, in an unexpected direction, and demonstrated the fact that the chlorine atom in chloroketodimethyltetrahydrobenzene is very reactive—a fact which greatly enhances the possibilities of the use of this and similar chloroketones for synthetical purposes. Small quantities of hydroxydimethylhexahydrobenzene (II.), but principally 3-*hydroxy*-5-*ethoxy*-1 : 1-*dimethylhexahydrobenzene* (IV.) were obtained, and it is evident that the sodium ethoxide formed in the first stages of the reduction reacts with the chlorine atom of the chloroketone to give the substance represented by Formula III., which is then further reduced to the corresponding saturated compound. The constitution of the latter is proved by analysis and by the facts that a Zeisel determination shows it to contain an ethoxy-group, and that, when treated with acetyl- or benzoyl-chlorides, it yields acetyl- or benzoyl-derivatives respectively.

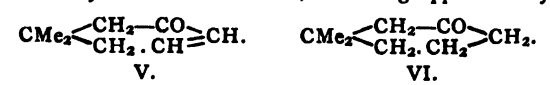


I. II.

III. IV.

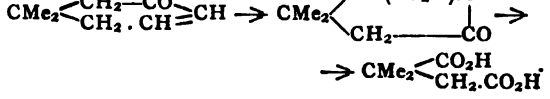
The main object of the investigation was, however, to find reducing agents, less powerful than sodium in moist ethereal solution, which would be discriminating in their action; so that it might be possible to prepare from chloroketodimethyltetrahydrobenzene, first, a ketodimethyltetrahydrobenzene, differing from the former only in that chlorine would be replaced by hydrogen, and, secondly, the corresponding ketodimethylhexahydrobenzene. Complete success has attended the experiments, and further work is in progress with the object of proving that the reactions are general ones.

The next reducing agent employed was zinc-dust in aqueous alcoholic solution, which, as previously shown (*Journ. Chem. Soc.*, 1905, lxxxvii., 1497; 1906, lxxxix., 43), readily replaces halogen by hydrogen in saturated hydroaromatic substances, but in the present instance its action is too powerful, as it gives a mixture of the ketones represented by Formulæ V. and VI., containing approximately

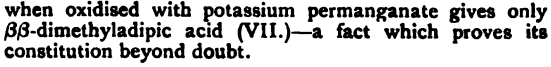


V. VI.

30 per cent of the latter. However, 3-*keto*-1 : 1-*dimethyl*-Δ^4-*tetrahydrobenzene* (V.) may be obtained quite pure by replacing zinc-dust by zinc-filings, either in the cold or on heating, or by using the zinc-copper couple. It is a colourless liquid boiling at 88·5° at 32 mm., and its ketonic nature is proved by the fact that it gives a semicarbazone and an oxime. When oxidised with potassium permanganate in the cold it yields *as*-dimethylsuccinic acid and the lactone of α-hydroxy-$\beta\beta$-dimethylglutaric acid :—



3-*Keto*-1 : 1-*dimethylhexahydrobenzene* (VI.) may be produced from chloroketodimethyltetrahydrobenzene by heating it with zinc-dust in glacial or dilute acetic acid solution. It is a colourless liquid boiling about 10° lower (75·5° at 25 mm.) than the corresponding unsaturated ketone. It forms an oxime and a semicarbazone, and when oxidised with potassium permanganate gives only $\beta\beta$-dimethyladipic acid (VII.)—a fact which proves its constitution beyond doubt.

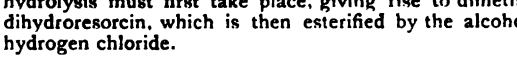


VII.

Other reducing agents investigated were zinc-dust in strongly alkaline solution, also zinc-dust and hydrogen chloride in alcoholic solution. In the former case the hydrolytic action of the potassium hydroxide overshadows the reducing action of the zinc, with the result that the only product isolated was dimethyldihydroresorcin (VIII.). In the latter case a mixture of ketodimethyltetrahydrobenzene and ketodimethylhexahydrobenzene was obtained,

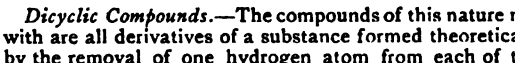
* Report of the Committee, consisting of Dr. E. Divers (Chairman), Prof. A. W. Crossley (Secretary), Prof. W. H. Perkin, Dr. M. O. Forster, and Dr. H. R. Le Sueur.

together with dimethyldihydroresorcin and its ethyl ether (IX.) (*Journ. Chem. Soc.*, 1899, lxxv., 775). Here, again, hydrolysis must first take place, giving rise to dimethyldihydroresorcin, which is then esterified by the alcoholic hydrogen chloride.

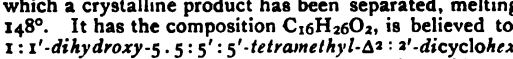


VIII. IX.

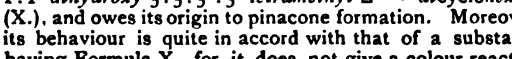
Dicyclic Compounds.—The compounds of this nature met with are all derivatives of a substance formed theoretically by the removal of one hydrogen atom from each of two hexahydrobenzene rings with consequent production of dicyclic derivatives. It has been decided to refer to this substance as di*cyclo*hexane, and to indicate the positions of the various substituting groups by adopting the following scheme of numbering :—



When zinc-dust acts on chloroketodimethyltetrahydrobenzene in aqueous solution there is obtained a mixture of ketodimethyltetrahydrobenzene and ketodimethylhexahydrobenzene (V. and VI.), in which the former largely predominates. If this mixture of ketones is again treated several times with zinc-dust, it is possible to isolate pure ketodimethylhexahydrobenzene and a semi-solid mass from which a crystalline product has been separated, melting at 148°. It has the composition $C_{16}H_{26}O_2$, is believed to be 1 : 1′-*dihydroxy*-5 . 5 : 5′ : 5′-*tetramethyl*-Δ^{2} : $2'$-di*cyclo*hexene (X.), and owes its origin to pinacone formation. Moreover, its behaviour is quite in accord with that of a substance having Formula X., for it does not give a colour reaction with concentrated sulphuric acid, nor can it be acetylated or benzoylated under the conditions employed. Further, its unsaturated nature is proved by the facts that it readily absorbs bromine, and when treated with sodium in moist ethereal solution it absorbs four atoms of hydrogen to give 1 : 1′-*dihydroxy*-5 : 5 : 5′ : 5′-*tetramethyldi*cyclo*hexane* (XI.). Here again this saturated pinacone does not give a colour reaction with concentrated sulphuric acid, but it is surprising to find that it is acetylated or benzoylated very readily, though no explanation of this fact can be offered on the present occasion.

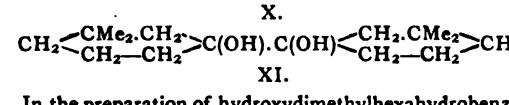


X.



XI.

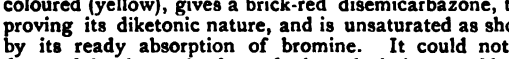
In the preparation of hydroxydimethylhexahydrobenzene considerable difficulty was experienced at one time in obtaining the product free from halogen, and on examining the resinous by-product formed under these conditions two solid substances were separated from it, melting respectively at 178° and 173—174°. The former of these has the composition $C_{16}H_{22}O_2$, and is apparently 3 : 3′-*diketo*-5 : 5 : 5′ : 5′-*tetramethyl*-Δ^{1} : $1'$-di*cyclo*hexene (XII.), formed by the direct coupling of two molecules of chloroketodimethyltetrahydrobenzene by the sodium. It is highly coloured (yellow), gives a brick-red disemicarbazone, thus proving its diketonic nature, and is unsaturated as shown by its ready absorption of bromine. It could not be detected in the resin formed when alcohol was added to the ether used in the reduction of chloroketodimethyltetrahydrobenzene, but much larger quantities of the second substance melting at 173—174°, and also another compound melting sharply at 212° were isolated. The latter proved to be identical with 1 : 1′-dihydroxy-5 : 5 : 5′ : 5′-tetramethyldi*cyclo*hexane (XI.).



XII.

For a long time the substance melting at 173—174° was thought to be homogeneous, as it gave on analysis numbers agreeing with the formula $C_{16}H_{30}O_2$, nor was its melting-point altered by many re-crystallisations, and, moreover, it sublimed in needles which melted at 171—172°. Nevertheless, it was found to be a mixture, for on acetylation it gave two diacetyl derivatives melting at 130° and 68°, and on benzoylation two dibenzoyl derivatives melting at 199° and 134°. The former of the diacetyl and dibenzoyl compounds (m. p. 130° and 199°) proved to be diacetyl- and dibenzoyl-1 : 1′-dihydroxy-5 : 5 : 5′ : 5′-tetramethyldi*cyclo*hexane, which substance they yielded on hydrolysis.

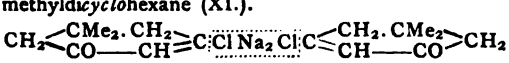
The above-mentioned derivatives melting at 68° and 134° were separately hydrolysed with alcoholic potassium hydroxide, when they each gave a substance, $C_{16}H_{30}O_2$, melting at 183°, which is believed to be 3 : 3-*dihydroxy*-5 : 5 : 5′ : 5′-*tetramethyldi*cyclo*hexane* (XIII.). It is readily acetylated and benzoylated, and, unlike the unsaturated or saturated pinacones, gives a decided colour reaction with sulphuric acid. Its formation would be due to the further reduction of diketotetramethyldi*cyclo*hexene (XII.). although, unfortunately, sufficient of the latter material could not be isolated to try the action of reducing agents upon it.



XIII.

The substance melting at 173—174° is therefore a mixture of 1 : 1′-dihydroxy-5 : 5 : 5′ : 5′-tetramethyldi*cyclo*hexane (XI.) and 3 : 3′-dihydroxy-5 : 5 : 5′ : 5′-tetramethyldi*cyclo*hexane (XIII.), and it would appear therefore that in the reduction of chloroketodimethyltetrahydrobenzene with sodium in moist ethereal solution dicyclic compounds are formed both by the process of pinacone formation and by the coupling reaction of the sodium.

2. *Action of Alcoholic Potassium Hydroxide on* 3-*Bromo*-1 : 1-*Dimethylhexahydrobenzene* (Crossley and Renouf, *Journ. Chem. Soc.*, 1906, lxxxix., 1556).—The preparation of 3-bromo-1 : 1-dimethylhexahydrobenzene (XIV.) has been previously described (*Ibid.*, 1905, lxxxvii., 1497), and also the action of alcoholic potassium hydroxide on this substance (*Ibid.*, p. 1499), which was stated to give rise to 1 : 1-dimethyl-Δ^{3}-tetrahydrobenzene (XV.) only,



XIV. XV.

and not to the isomeric tetrahydrobenzene with the double bond in the Δ^{2}-position. This conclusion, which was based on the result of oxidation experiments, was so unexpected that it appeared desirable further to investigate the supposed 1 : 1-dimethyl-Δ^{3}-tetrahydrobenzene, especially as there appeared to be a fairly easy means of deciding the point at issue. If this hydrocarbon has the constitution represented by Formula XV., then on treatment with bromine it would give rise to 3 : 4-dibromo-1 : 1-dimethylhexahydrobenzene (XVI.), which, on treatment with a

XVI. XVII.

reagent capable of removing the elements of hydrogen bromide, should yield 1 : 1-dimethyl-^{2} : 4-dihydrobenzene (XVII.) (*Journ. Chem. Soc.*, 1902, lxxxi., 832). But though the hydrocarbon obtained by the action of quinoline on the dibromodimethylhexahydrobenzene had the odour and gave the colour reaction characteristic of 1 : 1-dimethyl-Δ^{2} : 4-dihydrobenzene, it has been proved by analysis and a study of its oxidation products to be an undoubted mixture of dimethyldihydro- and dimethyltetrahydro-benzenes.

Being under the misapprehension that the dibromodimethylhexahydrobenzene, from which the mixture of hydrocarbons had been prepared, was a homogeneous

substance, the oxidation products expected were *as*-dimethylsuccinic acid, resulting from the oxidation of the dimethyldihydrobenzene, and *ββ*-dimethyladipic acid, from the oxidation of the dimethyltetrahydrobenzene.

$$CMe_2<\begin{matrix}CH_2.CHBr\\CH_2—CH_2\end{matrix}>CHBr \rightarrow$$
$$\rightarrow CMe_2<\begin{matrix}CH_2—CH\\CH_2.CH_2\end{matrix}\geqslant CH \rightarrow$$
$$\rightarrow CMe_2<\begin{matrix}CH_2.CO_2H\\CH_2.CH_2.CO_2H\end{matrix}$$

Instead there were actually obtained *aa*-dimethyladipic and *as*-dimethylsuccinic acids. This at once proved that the tetrahydrobenzene contained in the mixture of hydrocarbons must have been 1 : 1-dimethyl-Δ^1-tetrahydrobenzene, and therefore that the supposed 1 : 1-dimethyl-Δ^2-tetrahydrobenzene, which formed the starting-point of this investigation, was not a homogeneous substance, but consisted of a mixture of 1 : 1-dimethyl-Δ^1-tetrahydrobenzene and 1 : 1-dimethyl-Δ^2-tetrahydrobenzene. If this were so, then on oxidation a mixture of *aa*- and *ββ*-dimethyladipic acids would be obtained, and, as it had been

$$CMe_2<\begin{matrix}CH_2—CH\\CH_2.CH_2\end{matrix}\geqslant CH \rightarrow CMe_2<\begin{matrix}CH_2.CO_2H\\CH_2.CH_2.CO_2H\end{matrix}$$

$$CMe_2<\begin{matrix}CH=CH\\CH_2.CH_2\end{matrix}>CH_2 \rightarrow$$
$$\rightarrow CMe_2<\begin{matrix}CO_2H\\CH_2.CH_2.CH_2.CO_2H\end{matrix}$$

found possible, contrary to the statement of Blanc (*Bull. Soc. Chim.*, 1905, [iii.], xxxiii., 889), to separate these two acids (Crossley and Renouf, *Journ. Chem. Soc.*, 1906, lxxxix., 1552), a further quantity of 20 grms. of dimethyltetrahydrobenzene (*Ibid.*, 1905, lxxxvii., 1499) was prepared and oxidised with potassium permanganate (*Ibid.*, p. 1502). There was no difficulty in proving that the solid product obtained consisted of a mixture of *aa*- and *ββ*-dimethyladipic acids, in which the latter largely predominated, thus proving definitely the correctness of the above inference regarding the composition of the substance previously described as 1 : 1-dimethyl-Δ^1-tetrahydrobenzene.

It follows from the above evidence that the supposed 3 : 4-dibromo-1 : 1-dimethyl-hexahydrobenzene (Crossley and Renouf, *Journ. Chem. Soc.*, 1905, lxxxvii., 1501) is a mixture of this substance with the corresponding 2 : 3-dibromo-derivative. When treated with quinoline the former (XVIII.) loses the elements of hydrogen bromide to

$$CMe_2<\begin{matrix}CH_2.CHBr\\CH_2—CH_2\end{matrix}>CHBr \rightarrow CMe_2<\begin{matrix}CH:CH\\CH_2.CH\end{matrix}\geqslant CH.$$

XVIII.

give 1 : 1-dimethyl-$\Delta^{2:4}$-dihydrobenzene, which forms the main portion of the resulting mixture of hydrocarbons. But in the case of 2 : 3-dibromo-1 : 1-dimethyl-hexahydrobenzene (XIX.) the removal of the hydrogen bromide

$$CMe_2<\begin{matrix}CHBr.CHBr\\CH_2—CH_2\end{matrix}>CH_2 \rightarrow CMe_2<\begin{matrix}C\equiv C\\CH_2.CH_2\end{matrix}>CH_2$$

XIX. XX.

or—

$$CMe_2<\begin{matrix}CH=CH\\CH_2.CH_2\end{matrix}>CH_2.$$

cannot take place in an exactly similar manner, because the carbon atom to which the *gem*-dimethyl group is attached has no hydrogen atoms in connection with it. The reaction might take place, giving rise to a substance of Formula XX. containing a treble bond, or the two bromine atoms might be alone removed, possibly as a quinoline bromide. The former suggestion does not seem probable, because, although the hydrocarbon would give *aa*-dimethyladipic acid on oxidation, it would be isomeric with dimethyldihydrobenzene, but analysis showed the substance to be a mixture of dimethyldihydro- and dimethyltetrahydro-benzenes. In the latter case 1 : 1-dimethyl-Δ^2-tetrahydrobenzene would result, which would also give *aa*-dimethyladipic acid on oxidation, and, furthermore, its presence would be in agreement with the analytical data.

(To be continued).

ON THE NATURE OF VALENCY.*

By Prof. W. J. POPE and W. BARLOW.

THE modern developments of chemistry and crystallography indicate with ever increasing distinctness that the chemical atom, even when its individuality is shrouded by combination with other and different atoms, exhibits characteristics which are essentially its own and which are discernible in the compounds into which it enters. As chief among the attributes which an atom exhibits when present as a constituent of a compound molecule may be noted (1) its mass, (2) its space-occupying property or characteristic volume, and (3) its position property, or power of retaining occupation of a definite domain with respect to neighbouring atoms.

Nothing need here be said concerning the conservation of atomic mass; with regard to (2), the space-occupying property or characteristic volume of the atom, it may be remarked that the work done on molecular volumes has all had for its object the definition of conditions under which the atom of any particular element occupies the same volume when contained in different molecular complexes. The conception is thus involved that if a series of substances could be examined under absolutely corresponding conditions it would be found that those atoms common to the several substances would occupy the same absolute volume throughout the series. We have endeavoured to show in our work that if two elements are common constituents of a number of compounds, the relation between the volumes occupied by the atoms of those two elements remains practically constant during the passage from any one to any other compound of the series. As to (3), the conclusion that in a compound substance each component atom appropriates a certain domain of fixed position with respect to the other atoms composing the molecule, is established by the facts of stereochemistry and by the crystallographic facts connected with isomorphism and with morphotropic relationships.

A fourth attribute of the atom may now be mentioned, namely, the shape assumed by its domain. It is obvious that the second and third properties of the atom, those concerned with its volume and its arrangement, must play a large part in defining the shape of the space which it appropriates in a compound substance. Given the relative situations of the centres of the atomic domains and the relative volumes of those domains, the problem involved in the shape of the latter resolves itself into that of partitioning the space occupied by the substance, without leaving interstices, so as to allot to each atom its own polyhedral cell or domain throughout which its influence is predominant.

The object of the present communication is to demonstrate the possibility, in a great number of cases, of arriving at perfectly definite conclusions concerning the last three attributes referred to by using the data accumulated by chemists and crystallographers, and that a consequence of this is to prove that the fundamental valency of an element represents very approximately the number of units of volume contained in the polyhedral cell which constitutes the domain of its atom in any molecular assemblage. Valency thus stands revealed as primarily a simple volume relation, and this result is found to be in harmony with the various aspects of valency as illustrated by the composition and constitution of both organic and inorganic

* Paper forming the basis of a Discussion on this subject at the Leicester Meeting of the British Association (Section B), 1907.

compounds. The simplest possible assumption as to the form of the atomic domain or the sphere of atomic influence leads to results which are in most cases in immediate concordance with the experimentally determined facts, and, in other cases, leads to such a close approximation to concordance as indicates that any requisite modifying hypothesis is but subsidiary in character.

It is now known that all crystalline substances are distinguished by possessing homogeneity of structure, a homogeneous structure being described as one in which corresponding points continually recur about each of which the distribution of parts is the same. A number of facts indicate that in a crystalline substance the relative movements of the atoms or molecules composing the substance are performed about centres which occupy fixed positions; the atoms may indeed for most purposes be regarded as centres of attraction and repulsion, and the crystalline structure then becomes an equilibrium arrangement of such centres.

In the crystalline structure assumed by an element, provided that the identical component atoms do not form groups or molecular aggregates the constituent atoms of

Section on 100

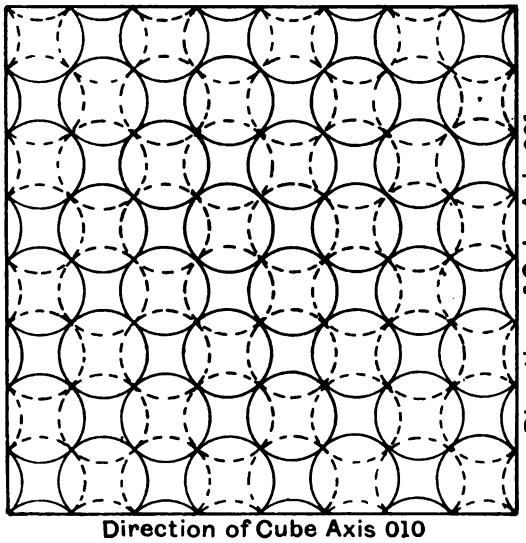


FIG. 1.

which have diverse situations, the polyhedral spaces appropriated by the atoms will be all alike; the simplest possible assumption which can be made as to the shape of these spaces or spheres of atomic influence is that they depart as little as possible from sphericity. The polyhedral cells must fill space without leaving interstices, and, according to the assumption referred to, the centres of the identical polyhedral cells will be those of the centres of a closest-packed assemblage of equal spheres.

As is well known, there are two varieties of homogeneous arrangement of equal spheres in closest-packing, all other equally close-packed arrangements being formed by intimate interstratification of these; they are distinguished as the cubic and the hexagonal closest-packed arrangements respectively. The cubic arrangement possesses holohedral cubic crystalline symmetry, and its plan, parallel to a cube face, consists of two alternating sections as shown in continuous and broken circles respectively in Fig. 1; the plan parallel to an octahedron face consists of three consecutive sections which are shown respectively as heavy, light, and broken circles in Fig. 2.

The hexagonal arrangement possesses holohedral hexagonal symmetry, and its plan on a plane parallel to the principal plane of symmetry consists of the two sections shown in Fig. 3; the axial ratio of the hexagonal closest-packed assemblage of equal spheres is either $a : c = 1 : 0{\cdot}8165$ or $1 : 1{\cdot}4142$, according to the direction selected for the axis a.

Section on 111

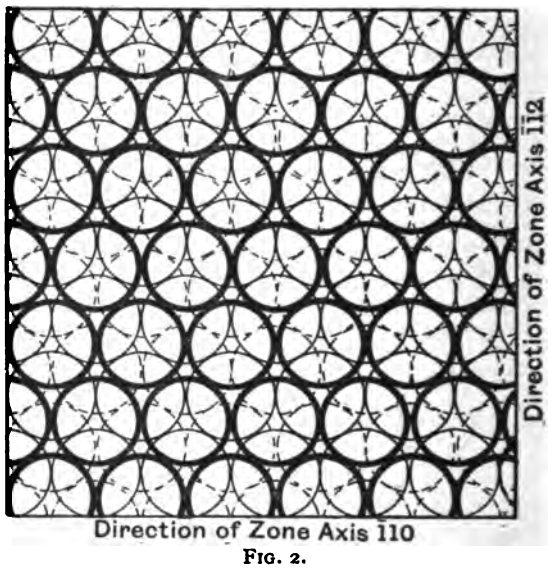


FIG. 2.

If these two closest-packed arrangements are built up of elastic and deformable, but incompressible, spheres, and the completed assemblages are subjected to sufficient uniform pressure from all sides to squeeze the spheres into the shape of polyhedra, all interstitial space will be eliminated, but the symmetry and relative dimensions of the arrangements will be preserved. Arrangements thus modified represent equilibrium assemblages of centres of attraction and repulsion in the cases where all these centres are similar.

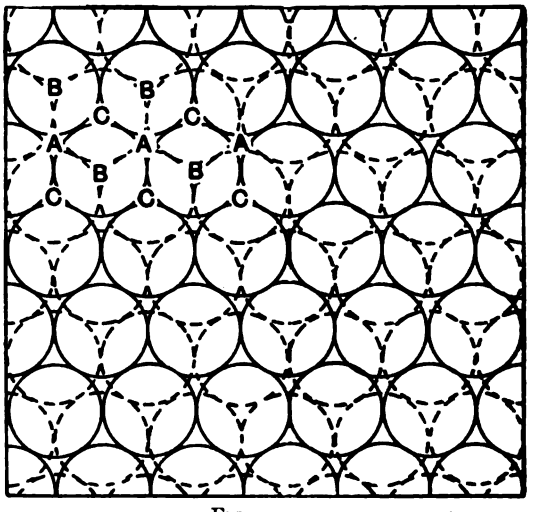


FIG. 3.

A crystalline element in which no molecular aggregation of the similar atoms occurs should thus exhibit holohedral cubic or hexagonal symmetry, and, in the latter case, the axial ratio would have one of the values stated above; that this is so is confirmed by the fact that of the 40 known

crystalline forms of the elements 20 are cubic and 14 are hexagonal, and that, in the cases of the latter, the axial ratios approximate to the theoretical values stated.

About six crystalline forms of elements are known which are neither cubic nor hexagonal; the operation of some factor additional to those already referred to must be assumed to account for their occurrence. Suppose that in the building up of the two closest-packed assemblages of equal spheres described, a form of aggregation of the spheres occurs which is comparable to molecular aggregation; unless this aggregation is strictly compatible with the formation of a cubic or hexagonal closest-packed assemblage, as the case may be, the packed assemblage

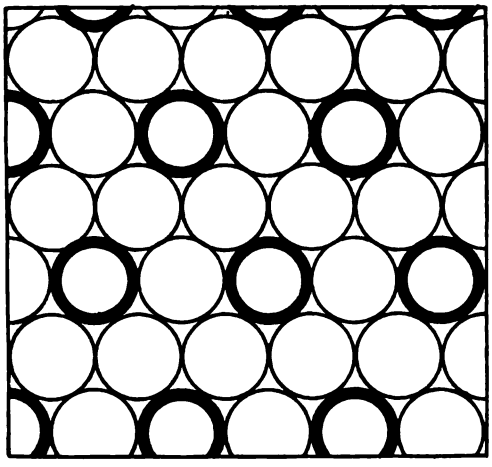


FIG. 4*a*.

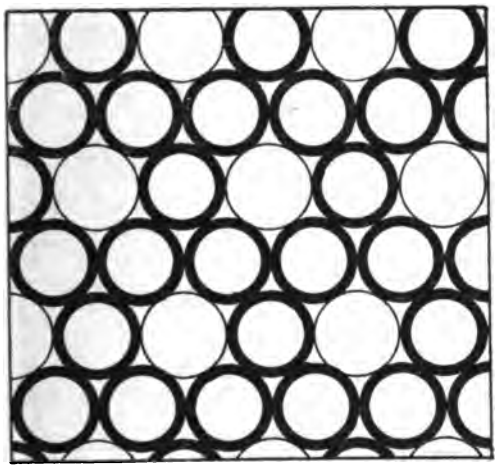


FIG. 4*b*.

will be one in which certain component spheres, homogeneously arranged, will receive slightly different treatment from the others. The conditions thus established could be simulated, so far as the general or crystallographic symmetry is concerned, by building up the appropriate assemblages from spheres possessed of slight polarity, from figures differing slightly from perfect spheres, or from two or more kinds of spheres nearly equal in size and present in definite numerical proportion. The arrangement, or the "marshalling," of the cubic or hexagonal closest-packed assemblage would still be retained, but the resultant assemblage would not be identical in symmetry and dimensions with that produced by using equal spheres.

The crystalline forms of those elements which are neither cubic nor hexagonal can be simulated in the manner thus indicated; they are, in fact, all either pseudo-cubic or pseudo-hexagonal. Thus, the monosymmetric form of sulphur showing $a : b : c = 0{\cdot}9958 : 1 : 0{\cdot}9998$, $\beta = 95°46'$, is obviously pseudo-cubic, and the orthorombic iodine, which shows the axial ratios, $a : b : c = 0{\cdot}6644 : 1 : 1{\cdot}3653$, is also pseudo-cubic because the axial ratios given are almost precisely in the ratio of $a : b : c = 2 : 3 : 4$.

On turning next to binary compounds composed of two elements of the same valency, it is found that practically all of these are either cubic or hexagonal in crystalline form. The following is a complete list of the axial ratios of the known hexagonal members of this class, from which it will be seen that all approximate very closely to the form of axial ratios, $a : c = 1 : 0{\cdot}8165$ or $1 : 2 \times 0{\cdot}8165$, of the hexagonal closest-packed assemblage of equal spheres. The cubic and hexagonal forms of the binary compounds of two elements of the same valency are, however, not all holohedral in crystalline symmetry.

BeO	..	..	$a : c = 1 : 1{\cdot}6305$
ZnO	..	..	$a : c = 1 : 1{\cdot}6077$
ZnS	..	..	$a : c = 1 : 0{\cdot}8175$
CdS	..	..	$a : c = 1 : 0{\cdot}8109$
AgI	..	..	$a : c = 1 : 0{\cdot}8196$

It is convenient to term the space occupied by each sphere in the uncompressed assemblage plus a proportionate

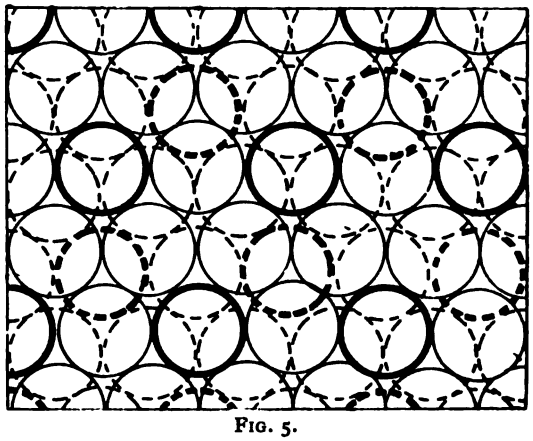


FIG. 5.

share of the interstitial space, or by each polyhedron in the compressed assemblage, the sphere of influence of an atom of the element concerned. By assigning to the two constituent elements of any of the binary compounds just mentioned spheres of atomic inflence of approximately the same volume, it is obvious that assemblages may be built up which will exhibit the axial ratios quoted above. Homogeneous assemblages representative of the cubic or hexagonal binary compounds in question can be constructed from spheres of two kinds, but of approximately equal volume, present in equal numbers; in every case the hemihedrism shown by the binary compound can be accounted for by the slight difference in size between the spheres of atomic influence of the two elements concerned. This has been worked out in detail in the case of the gyrohedrally hemihedral cubic alkali halogen salts and the hemimorphously hexagonal silver iodide. The assemblages thus constructed present geometrical properties which are entirely in harmony with corresponding physical properties of the crystalline material. The cleavage, twinning, and gliding of the cubic alkali halogen salts and the dimorphism of silver iodide are quite precisely paralleled by corresponding properties of the assemblages suggested as representing the crystalline structures of these salts.

The crystal structure of the binary compound is, in all

the preceding cases, derived by packing together triangularly arranged layers of the same pattern in either cubic or hexagonal symmetry; these layers are made up of two sorts of spheres and are of two kinds, as indicated in Fig. 4, *a* and *b*. One sort of sphere, say that marked heavily, represents the sphere of influence of the metallic atom; the other, which is marked lightly, represents the other element present in the binary compound. Since in the first layer, say Fig. 4*a*, only one-fourth of the total number of spheres represent metallic atoms, it should be possible to derive assemblages representing the tri-halogen compounds of the alkali metals, such as RbI_3, by arranging identical layers of this kind in close-packing. An appropriate mode of packing such layers is shown in Fig. 5, which represents an assemblage in which three principal dimensions can be distinguished as lying in three principal directions mutually at right angles; the values of the corresponding dimensions in these directions, if all the spheres are equal, are as—

$$a : b : c = 1 : 2\sqrt{\tfrac{2}{3}} : \sqrt{3}$$
$$= 0{\cdot}6124 : 1 : 1{\cdot}0608.$$

These values approximate to those obtained as the axial ratios of the orthorhombic tri-halogen compounds of the alkali metals, a few of which are next stated :—

	a :	*b* :	*c*	*x* :	*y* :	*z*
RbI_3	0·6858 :	1 :	1·1234	1·1875 :	1·7316 :	1·9452
CsI_3	0·6825 :	1 :	1·1051	1·1901 :	1·7440 :	1·9273
TlI_3	0·6828 :	1 :	1·1217	1·1846 :	1·7350 :	1·9461
Ideal values	0·6124 :	1 :	1·0608	1·1224 :	1·8239 :	1·9443

The values last quoted, conveniently termed the ideal values, refer to the structure composed of two kinds of spheres of equal size, the one kind being three times as numerous as the other. (The values *x*, *y* and *z* given in the table represent the so-called equivalence parameters; they satisfy the conditions that $x : y : z = a : b : c$ and $x \times y \times z = W$; W being the sum of the valencies of the atoms composing the molecule). If the two kinds of sphere are not of exactly the same size, it can be shown that the values of *a* or *x* should be greater according as the difference between the two sizes is greater, and that the minimum value, 0·6124 or 1·1234, would only be attained with two kinds of spheres of identical volume. Similarly the magnitude *y* should assume a maximum value in the ideal assemblage, and any difference in volume between the two kinds of spheres should result in a diminution of the *y* value to less than the maximum value of 1·8239. These conditions are fulfilled in the cases of all the measured compounds, 16 in number, of the type under discussion; the *x* value is always greater, and the *y* value always less, than those holding for the ideal assemblage of equal spheres.

From a consideration of the axial ratios and the equivalence parameters of the alkali trihalides it is concluded that the spheres of atomic influence of the monovalent elements concerned have not exactly the same volumes, but that the relation in size is of the following kind :—

Cl less than Br and Br less than I.

K less than Rb, Rb nearly equal to Tl, and less than Cs.

This kind of relation is found to hold consistently throughout numbers of compounds, and is traceable in series of quite different types to the substances under discussion. Thus Tutton has recently shown that the orthorhombic rubidium and thallous sulphates (or selenates) exhibit axial ratios which are more nearly alike than those of the corresponding salts of potassium, rubidium, and cæsium. Evidence is also available that the sphere of atomic influence of fluorine is smaller than that of chlorine, and in accordance with this it is to be noted that the compounds SF_5 and SCl_4 are those in which sulphur is combined with the maximum proportion of the halogen element.

(To be continued).

NOTICES OF BOOKS.

A Text-book of Botany and Pharmacognosy. By Henry Kraemer, Ph.B., Ph.D. Second Edition. Philadelphia and London: J. B. Lippincott Company.

In the first part of this book the distinguishing characters of the main groups of plants, their morphology and histology, are discussed in detail, a certain amount of plant physiology being also introduced. The points in which students of pharmacy and medicine are specially interested are emphasised, and a chapter is devoted to the cultivation of medicinal plants; full lists are given of those medicinal plants which grow wild in America and of those which already are, or might profitably be, cultivated. The second section deals with pharmacognosy, and opens with descriptions of crude drugs, their constituents and adulterants, together with directions for collecting and preserving them. In the second chapter of this part a system of classification of powdered drugs and foods is given, and their identification is made as simple as possible, so that analysts will find that the book is a valuable aid to them in this difficult and important branch of their work. The third section gives a short account of the reagents required for microscopical work and the preparation and staining of sections. The book is particularly fully and well illustrated, and for students of pharmacy and medicine it has a great value as a comprehensive text-book.

Forty-third Annual Report on Alkali, &c., Works. By the Chief Inspector. London: Wyman and Sons. Edinburgh: Oliver and Boyd. Dublin: E. Ponsonby. 1907.

The general and detailed reports of the work done during 1906 under the provisions of the Alkali, &c., Works Regulations Acts are supplemented in this volume by a full account of researches on the constitution of ammoniacal liquors. It has been found that in the main the methods hitherto adopted have given satisfactory results, and they are still employed with some slight modifications. The process for the estimation of thiocyanate has, however, undergone a complete revision, and a method has now been worked out which is decidedly more accurate than the original procedure, and has the advantage of being quickly performed. Full details of this new method are included in the Reports. The temperature of carbonisation in coke ovens and gas retorts has also been the subject of investigation, and reproductions are given of graphical records from one of the coke ovens in Brackley Colliery, as well as the temperature charts from a paper read by Mr. J. Bond, engineer and manager of the Southport Corporation Gas Works, before the Institution of Gas Engineers, in May, 1905.

Denatured or Industrial Alcohol. By Rufus Frost Herrick. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1907.

In January, 1907, a law permitting the use of tax-free denatured alcohol came into force in the United States, and accordingly this book will have a special interest for American chemists, engineers, and manufacturers, and even for the general public. The author gives a full account of the manufacture, distillation, and rectification of alcohol, and describes methods of examining it for impurities, while its use as an illuminant is carefully compared with that of acetylene. In describing the various burners, stoves, &c., which are adapted for alcohol, and the machines in which it is used as a source of power, the author has been obliged to illustrate chiefly foreign machinery, Germany especially having been in the forefront in developing this kind of apparatus, although now the internal revenue tax has been removed in America in all probability the next few years will see great increases in its employment in the United States. A considerable part of the book is devoted to the laws and regulations for

denatured alcohol now in force, and a useful list of patents relating to its manufacture, and to various modifications of distilling apparatus is included.

Traité Complet d'Analyse Chimique Appliquée aux Essaies Industriels. ("Treatise on the Chemical Analysis of Industrial Products") By J. POST and B. NEUMANN. Translated by Dr. L. GAUTIER. Vol. I., Part I. Paris: A. Hermann. 1907.

THE Second French Edition of this comprehensive treatise has been prepared from the enlarged Third German Edition, now in course of publication, by Dr. Gautier, who has made some important additions to the text. The first part of Vol. I. contains sections on the analysis of water by Dr. J. H. Vogel, on fuels by Dr. H. Langbein, and on pyrometry and the analysis of gases from furnaces, chimneys, mines, &c., by Prof. Neumann. The illustrations of the original have been carefully reproduced, and the work will be cordially welcomed by French technical chemists.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlv., No. 2, July 8, 1907.

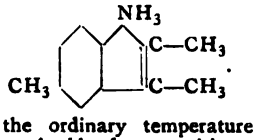
Preparation and Properties of Borides of Iron, Fe_2B and FeB_2.—Binet du Jassonneix.—Mixtures of varying proportions of iron and boron were heated in a magnesia boat in a porcelain tube through which a current of hydrogen was passed. Mixtures which are infusible at the temperature at which porcelain begins to soften were heated in magnesia crucibles in the electric furnace. The melts obtained looked crystalline when up to 7 per cent of boron was present. The surface and fracture showed long prismatic needles, which could be isolated by allowing cold dilute hydrochloric acid to act upon the melt for some time. These crystals have the formula Fe_2B. When the percentage of boron was above 7 the crystallisation appeared less regular. Melts with about 9 per cent of boron appeared homogeneous, and were completely dissolved by cold hydrochloric acid. The boride Fe_2B consists of steel-grey crystals; its density at 18° is 7·37; it oxidises in dry air only at a red heat, but in damp air it is rapidly altered; it dissolves very slowly in dilute or concentrated hydrochloric and sulphuric acids when warmed, but is not attacked by the cold acids. Warm dilute nitric acid dissolves it, and the concentrated acid attacks it very rapidly in the cold. The compound FeB_2 when prepared in an electric arc furnace contains a large amount of carbon boride. When most of this is removed a metallic powder is obtained; it is not attacked either by hot or cold dilute hydrochloric acid; the concentrated acid slowly attacks it when heated; nitric acid dissolves it easily, leaving a residue of carbon boride; it is oxidised slowly in the air.

Direct Oxidation of Toluene by Catalysis.—Paul Woog.—When a current of air containing toluene is passed over a hot platinised mass, made by impregnating fragments of meerschaum (previously washed with acids) with a platinum salt, then reducing the latter and washing, energetic oxidation takes place, and the toluene is completely burnt to carbon dioxide and water, provided that the temperature is sufficiently high to prevent the toluene condensing. When iron oxide is used as catalyser at temperatures from 175—300° benzaldehyde is regularly formed, the best yield being obtained when the tube is raised to a temperature of 280° and the toluene to 90°. Above 280° the iron oxide becomes incandescent and some carbonaceous matter is obtained. Under the same conditions nickel oxide gives rise to benzaldehyde at 150°. Above 230° small quantities of phenolic substances are obtained, and may be detected by their smell and by means of Millon's reagent. The nickel oxide becomes incandescent at 270°. Copper oxide gives a certain amount of benzaldehyde, but most of the toluene is burnt, the oxide becoming incandescent above 250°. With manganese dioxide the hydrocarbon is completely burnt. If carbon, in the form of coke, is used as a catalyser, a little aldehyde is produced at 200°, but the chief product of the oxidation is benzoic acid, large quantities being formed at 370°.

New Method of Preparing Amino-alcohols with Primary Alcoholic Function.—H. Gault.—The author has prepared ethyl glycocollate, benzyl, phenyl, *m*- and *p*-tolyl, methyl phenyl aminoacetic esters, and β-diethylaminopropionic ester by the direct condensation (except in the first case) of ethyl chloracetate or β-chlorpropionate with the corresponding amines—a method which gives excellent results, the amino-ester being obtained quantitatively. When these esters are reduced by sodium and absolute alcohol, the directions of Bouveault and Blanc being carefully followed, varying yields of the corresponding amino-alcohols are obtained, except in the case of ethyl glycocollate and ethyl *m*- and *p*-tolyl acetates, and thus, though the reduction of these esters is not effected when the amine function is primary, this method may with advantage be employed to prepare primary amino-alcohols when the amine function is secondary or tertiary.

Asymmetric Derivatives of Hexane-diol 1 : 6. Heptamethylene Glycol. — R. Dionneau.—To prepare the bromo-ethers of hexane-diol of the formula $RO(CH_2)_6Br$, it is best to allow one molecule of alkaline alcoholate to react upon one molecule of dibromohexane in anhydrous ether, $CH_3ONa + Br(CH_2)_6Br = NaBr + CH_3O(CH_2)_6Br$. The reaction occurs at the temperature of the room, and the crystals of sodium bromide are deposited at the end of a day. When they begin to appear, the mixture is warmed gently and the ether layer distilled off. At 112° methoxybromohexane 1 : 6 distils over. The magnesium derivative, $BrMg(CH_2)_6OCH_3$, when treated with bromomethyl ether, $BrCH_2OCH_3$, gives the dimethyl derivative of heptane diol, $CH_3O(CH_2)_7OCH_3$. This, when heated to 100° with hydrobromic acid, gives dibromoheptane 1 : 7, from which diphenoxyheptane can be prepared by the action of sodium phenolate. Dibromoheptane when treated with silver acetate is transformed into the diacetic ether, which gives heptamethylene glycol when distilled over soda-lime.

Action of Halogen Derivatives of Acetones upon Aromatic Amines.—A. Richard.—When monochlordimethyl acetone reacts with two molecules of aniline warmed on a water-bath, aniline chlorhydrate is formed, and a viscous brown substance, which dissolves in hydrochloric acid and in alcohol. If the alcoholic solution is thrown into cold water a chesnut-brown precipitate is formed, which appears to be a phenyl acetone amine of the formula $N\begin{cases}H\\C_6H_5\\CH_2—CO—CH_3\end{cases}$. The reaction occurs similarly when one of the three toluidines is substituted for aniline, the product being $N\begin{cases}H\\C_6H_4.CH_3\\CH_2—CO—CH_3\end{cases}$. In no case did the author obtain the indolic derivative described by Vladesco. When α-chlor or α-brom methyl ethyl acetone is heated with aniline or *p*-toluidine, crystalline products are obtained. One of these has already been described by Vladesco, but the other has the formula $C_{10}H_{11}N$, or—



Apparently, at the ordinary temperature the reaction which occurs is a double decomposition. The halogen combines with one atom of the hydrogen of the amine employed, giving a hydracid which forms a salt of the

amine, while the ketone residue takes the place of the hydrogen atom. If this ketonic amine is heated, and if the group $-N<^{H}_{R}$ is in the secondary position with regard to the group —CO— (as in the case of α-chlormethyl ethyl acetone), a more extensive condensation occurs, and one molecule of water and an indol derivative are formed.

— —

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xl., No. 11, 1907.

Anodic Disturbances in the Electrolysis of Fused Salts.—K. Arndt and K. Willner.—When a current is passed through fused barium chloride in a porcelain crucible, using thick iron wire as cathode and a carbon rod as anode, the resistance of the bath steadily increases after a few minutes, and the evolution of chlorine ceases. The same thing happens when strontium chloride is similarly treated, while calcium chloride can readily be electrolysed without exhibiting the phenomenon. If the anode is moved about it is possible to cause more chlorine to be generated. This difference in the behaviour of barium and strontium, on the one hand, and calcium on the other, cannot be ascribed to the higher melting-points of the two first elements, because the disturbance does not occur when calcium chloride is artifically superheated; nor can it be explained by the difference in the conductivity of the salts, which, though considerable, is not sufficiently large to cause the phenomenon. It was found, however, that the carbon was surrounded by a salt crust, which contained small quantities of silicic acid. This must have been derived from the crucible, for the strontium chloride used contained only 0·02 per cent silicic acid. Thus, when the melt became alkaline it attacked the porcelain, yielding silicates. When a crucible made by a substance containing no silica (*e.g.*, magnesia) was used, the resistance of the bath, although it rose for a moment, sank again, and then remained normal, and metallic strontium was formed in a compact mass. The introduction of a small amount of silica at once increased the resistance. Hence there can be no doubt that the formation of a badly conducting layer of silicic acid is the true cause of the anodic disturbance. Fused calcium chloride dissolves about 4 per cent of silica, while strontium chloride takes up much less. Also the more strongly alkaline strontium attacks the crucible more.

Proof of Divalence of Beryllium. Beryllium Picrate.—B. Glassmann.—When pure picric acid is dissolved in water, warmed, neutralised with beryllium carbonate, filtered, and evaporated to crystallisation, a yellow picrate crystallises out. When dried in air and analysed the formula is found to be $[C_6H_2(NO_2)_3O]_2Be+3H_2O$. If this picrate is treated with ether and dried at 50° it gives up one molecule of water. The molecular weight of the anhydrous picrate was determined by the freezing point method in acetophenone, care being taken that the latter was absolutely free from water. The molecular weight was found in two experiments to be 465 and 471·1, while the calculated value is 465·1. Thus the divalence of beryllium is confirmed by this work. When the anhydrous picrate is treated with water it gives a basic picrate of the formula $[C_6H_2(NO_2)_3O]_2Be.2OBe(OH)_2$.

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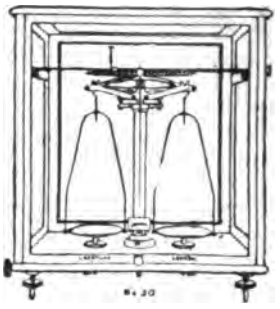

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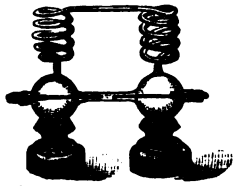
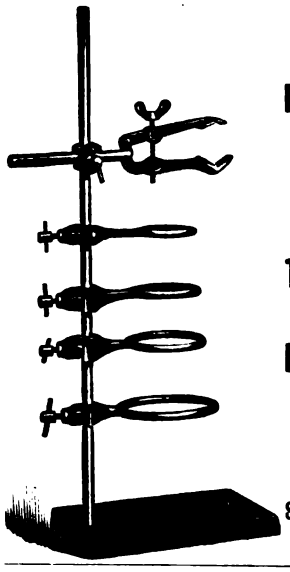


Hittorf's Tube showing the resistance of the dark space.



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THE CHEMICAL NEWS.

VOL. XCVI., No. 2491.

COPPER MIRRORS.*

By F. D. CHATTAWAY.

THE importance from the point of view of the health of the workpeople of obtaining a substitute for the tin amalgam used in the manufacture of mirrors has led many chemists to study the conditions under which metals are deposited from aqueous solution. These investigations have, however, usually had for their object the preparation of a liquid which would deposit a uniform and coherent layer of silver over a large glass surface at the ordinary temperature. Liebig was the first to solve this problem satisfactorily, and his method in which milk sugar is the reducing agent was formerly extensively used.

Other metals are not so easily deposited, and copper, which from its close relationship with silver one would expect to behave similarly, has never been observed to be so laid upon glass. Although copper mirrors have never been obtained by deposition of the metal from an aqueous solution, Faraday (*Phil. Trans.*, 1857, p. 145), about the time when silver mirrors were attracting much attention, made the interesting observation that a mirror-like deposit could be obtained by dissolving a little oxide of copper in olive oil and heating plates of glass in a bath of this liquid up to the temperature at which the oil decomposes. The mirrors, however, obtained by Faraday's method, if of any size, are liable to be stained or discoloured in patches by decomposition products of the oil, and they are, moreover, generally lacking in brilliancy. Further, as the deposition of the metal only takes place when the oil decomposes, the process is excessively disagreeable to carry out; and since the oil is spoiled it is also somewhat costly.

In the course of an investigation on the oxidation of aromatic hydrazines, the author made the observation that when solutions of cupric oxide are reduced by these compounds the metal is deposited upon the glass in the form of a brilliant coherent film if clear vessels are used.

The mirrors obtained by this method are very beautiful, as they show the lustrous red colour of burnished copper, and are as perfect in reflecting surface and as uniform as the similar mirrors obtained by the deposition of silver.

It seems probable that this method of depositing copper upon glass could receive important application in the production of objects of art.

CAUSES OF THE QUALITY STRENGTH IN WHEATEN FLOUR.†

By A. E. HUMPHRIES.

THE Home-grown Wheat Committee of the National Association of British and Irish Millers has for several years been engaged in producing wheats in England which shall yield maximum crops of grain and straw, the wheat to be equal in strength, and therefore in commercial value, to the best imported varieties.

The field of inquiry has been a wide one, and among other things the Committee has sought to ascertain "the ultimate cause of strength in wheat, the nature and source of those constituents which confer on some varieties of wheat the inherent quality of strength, and the power of transmitting it to succeeding generations." It has been proved that though climate and soil influence quality they are not the determining factors in the production of strength, for though the strongest wheats are ordinarily produced in districts where the winters are cold, the summers hot, and the summer rainfall high, certain varieties possess and retain the inherent quality of strength when grown in England. Manuring or early cutting at harvest time has no beneficial effect on quality. Quick growth or rapid maturation is not correlated with strength nor does the percentage of natural moisture in well-harvested wheat indicate it; indeed, in certain cases the addition of water to wheat materially increases its effective baking strength.

The term "strength" has been loosely applied to cover several characteristics. In the view of the Committee it should not be measured by the quantity of water required to make doughs of a standard consistency, nor by the quantity of bread produced per sack of flour used, nor by the way a flour behaves in the dough, but by its capacity for making big, shapely, and therefore well aërated loaves. This definition covers two characteristics; one, a flour's capacity for making gas in yeast fermentation; the other, its capacity when made into dough for retaining the gas so generated.

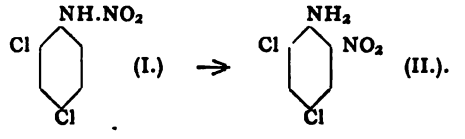
The gas-making power will depend largely on the percentage of natural sugar any given wheat contains and its diastatic capacity. These characteristics vary substantially in different wheats. The baker can, and does, influence the quantity of gas generated in baking. The retention of gas when made involves complex problems.

The percentages of total nitrogen, gluten, gliadin, and amyloids do not correctly indicate the relative strengths of various flours. The theory that strength depends on a correct ratio between gliadin and glutenin is untenable. Professor Wood's suggestion that the gas-retaining power of a dough depends on its ratio of protein to salts is worthy of the closest attention in view of the fact that the physical, as distinct from the chemical, properties of proteins are profoundly affected by small quantities of acids, alkalis, and salts.

THE TRANSFORMATION OF AROMATIC NITROAMINES AND ALLIED SUBSTANCES, AND ITS RELATION TO SUBSTITUTION IN BENZENE DERIVATIVES.*

I. *Nitroamines.* (*With* W. W. REED, B.Sc.).

A DETAILED study of the conditions governing the transformation of 2 : 4-dichloro-1-nitroaminobenzene (I.) (Orton, *Trans. Chem. Soc.*, 1902, lxxxi., 802) into the isomeric 2 : 4-dichloro-6-nitroaniline (II.) has been made:—



This nitroamine was chosen for particular study in preference to others, having different positions vacant (ortho and para relative to the group, $NH.NO_2$) into which the nitro-group may "wander," on account of the ease of its preparation (Orton, *Ber.*, 1907, xl., 370), and the non-basic character of the nitroaniline, of the above constitution, which is produced in the isomeric change. In testing the effect of minute quantities of acids as transforming agents it is of great importance that the aniline should not be able to unite with the reagent, which would thus be withdrawn from the sphere of action.

* A Paper read before the British Association (Section B), Leicester Meeting, 1907.

† Paper forming the basis of a Discussion on this subject at the Leicester Meeting of the British Association (Section B), 1907.

* Report of the Committee, consisting of Prof. F. S. Kipping (Chairman), Prof. K. J. P. Orton (Secretary), Dr. S. Ruhemann, Dr. A. Lapworth, and Dr. J. T. Hewitt. Read before the British Association (Section B), Leicester Meeting, 1907.

A particular advantage which this transformation offers, in contrast to many others of a similar type, is due to the fact that the nitroamine is quite colourless, and forms colourless solutions, which may be preserved for long periods, whereas the nitroaniline crystallises in intensely yellow needles and forms highly coloured solutions. Traces of the nitroaniline could thus be recognised, not only in solutions, but also in the crystals of the nitroamine. The conversion of the crystalline nitroamine into the nitroaniline is not merely indicated by a simple change of colour, but by the growth of yellow needles of the nitroaniline, apparently out of the colourless nitroamine—a process which can be readily followed photographically. This phenomenon, which can be demonstrated with a single crystal of the nitroamine, has allowed of the testing of the effect of single (necessary gaseous) reagents as transforming agents in the absence of all solvent.

The nitroamine was dried by sealing it up with phosphorus pentoxide in glass tubes. When thus entirely freed from water the substance acquires greater stability, and loses a remarkable sensitiveness to light, which necessitates the use of a dark room when aqueous solutions are employed.

After seven days' drying in this manner the tubes were opened, the reagent introduced, and the tube re-sealed. The reagent, which was in most cases in aqueous solution 0·1 to 0·2 cc.), was enclosed in a small tube, and was separated from the dried nitroamine by a column of phosphorus pentoxide five to six inches in length. The water slowly evaporated, and was absorbed by the pentoxide, the gaseous reagent, now anhydrous, diffusing to the region containing the nitroamine, of which at most one or two crystals (plates or needles) were used. Obviously this procedure admits only of the use of reagents which are not changed by prolonged contact with phosphorus pentoxide.

By this means it has been ascertained that hydrogen chloride, bromide, and iodide, nitric acid, chlorine, or bromine can all act as transforming agents. Iodine, hydrogen cyanide (?), sulphur dioxide, carbon dioxide, and methyl iodide are inactive.

Quantitative experiments carried out with hydrogen chloride have revealed the very interesting fact that there is a limiting concentration (partial pressure) below which hydrogen chloride does not initiate the molecular rearrangement. In the case of the nitroamine here dealt with the partial pressure of the hydrogen chloride must be approximately one-thirtieth atmosphere.

The behaviour of the nitroamine with hydrogen chloride in various solvents was investigated, the most instructive results being obtained in aqueous solution. The solution of the nitroamine in pure water can apparently be preserved indefinitely in a dark room, no trace of colour becoming perceptible, notwithstanding the fact that it is easy to perceive the colour communicated by 1/10 mgrm. of the nitroaniline to 100 cc. of the solution; that is, to detect the transformation of 0·1 per cent of the nitroamine. The addition of hydrogen chloride causes transformation, provided that the acid is above a certain concentration. The nitroamine was used at a concentration of V = 207 (1 grm. per litre), the concentration of the acid being varied from N to N/1000. In all the solutions but that last mentioned, in which the molecular ratio $C_6H_3Cl_2.NH.NO_2HCl$ was 5/1, the acid was in excess. The presence of the nitroaniline can be detected with certainty at the end of ten minutes in the N solution, and after longer periods down to a concentration of N/200, below which concentration all change ceases. Similar results were obtained with other acids, but, keeping the concentration of the nitroamine constant, the limiting value of the effective concentrations of the acids varies with the strength of the acid.

In the hope of isolating some compound of the acid and the nitroamine, hydrogen chloride, accurately dried, was passed into a solution of the nitroamine in petroleum. A colourless compound separated, which was resolved by solutions of alkalis into the nitroamine and hydrogen chloride, but when kept in a dry atmosphere the compound slowly changed into the nitroaniline.

These remarkable results greatly illuminate the mysterious part played in this type of intramolecular change by the transforming agent (or catalyst), the necessity for the presence of which was first recognised by Armstrong (*Report*, 1899, p. 683; and *cf. Trans. Chem. Soc.*, 1900, lxxvii., 1053).

The deductions to be drawn from these observations may be thus summarised:—

i. No "specific" reagent is required for any given transformation.

ii. The reagent must be capable of combining with the nitroamine. In all probability this union is effected directly with the nitrogen of the NH group, which thus becomes quinquivalent. The additive product in the case of hydrogen chloride has a composition represented by the formula $C_6H_3Cl_2.NH.NO_2,HCl$.

iii. No transformation occurs in aqueous solution when the concentration of the transforming agent is below a certain value (for hydrochloric acid below N/200), the nitroamine being at a dilution of V = 207. The additive compound is apparently completely "hydrolysed" at such dilution.

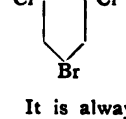
iv. The additive compound is not formed from gaseous hydrogen chloride and the nitroamine when the pressure of the former is below a certain value—namely, the dissociation pressure of the compound. This pressure is approximately one-thirtieth atmosphere at 15° C.

It has been suggested that the additive compound of the nitroamine and the transforming agent is alone capable of undergoing those further changes, probably through the transitory conversion of the benzene nucleus into a quinonoid form, by which the nitro-group "wanders" from the nitrogen into the nucleus, whereas the simple nitroamine has no such power (see Orton, *Proc. Roy. Soc.*, 1901, lxxi., 153).

II. *The Wandering of Bromine in the Chlorination of Bromoanilines.* (*With* W. W. Reed, B.Sc.).

Although the replacement of bromine by chlorine in anilines (Wegscheiden, *Monatsheft*, xviii., 329; Chattaway and Orton, *Trans. Chem. Soc.*, lxxix., 822), and in bromobenzenediazonium chlorides (Hantzsch, *Ber.*, xxx., 2334), has been observed, the displacement of bromine by chlorine from a given position in the benzene nucleus, followed, however, by a subsequent re-entry in another position, has not been described.

In the chlorination of *p*-bromoaniline, either by the usual method of passing chlorine into a solution in benzene or chloroform, or by the more delicate procedure of adding the requisite quantity of a solution of chlorine, or, finally, by using solutions of the aniline and chlorine (in the correct proportions, $C_6H_4Br.NH_2/2Cl_2$) in 20 per cent hydrochloric acid, the expected 2 : 6-dichloro-4-bromoaniline—



is not alone obtained. It is always mixed with 2 : 4-dibromo-6-chloro- and *s*-trichloro-anilines, and cannot be separated from them. The aniline can, however, be prepared in a pure state by indirect chlorination of the *p*-bromoaniline in chloroform solution with a solution of 2 : 4-dichloroacetylchloraminebenzene in the same solvent, thus:—

$$C_6H_4Br.NH_2 + 2C_6H_3Cl_2.NCl.AC = C_6H_2Cl_2Br.NH_2 + 2C_6H_3Cl_2.NH.AC.$$

Under these conditions displacement of bromine does not occur.

Similar results were obtained by chlorinating 2 : 4-dibromoaniline in hydrochloric acid solution. On subjecting *o*-bromo-, *m*-bromo-, or 2 : 6-dibromo-aniline to a similar treatment no such displacement was observed, each substance yielding a single chloro-derivative.

DYNAMIC ISOMERISM.*

ATTENTION has been directed during the past year mainly to a study of the influence of impurities on the velocity of mutarotation of nitro-camphor. In an earlier series of experiments on glucose it was found that the mutarotation in aqueous solutions could not be retarded by the addition of either acids or alkalis (Lowry, *Trans. Chem. Soc.*, 1903, lxxxiii., 1314—1323): the isomeric change thus appeared to be due to a direct interaction between the sugar and the water of low conductivity which formed the solvent. In the case of nitrocamphor dissolved in chloroform it has been found possible to check the mutarotation by the addition of N/100 acetic acid, and to stop it altogether during a period of three weeks by the addition of N/1000 trichloracetic acid. The experiments, therefore, afford valuable confirmation of the view already arrived at, that the isomeric change which usually takes place when nitrocamphor is dissolved in chloroform or benzene does not occur spontaneously, but is conditioned by the presence of *minute traces of alkaline impurities* (*Trans.*, 1899, lxxv., 221; *Report*, 1904, p. 196).

Experiments were made to determine quantitatively the effects produced by these impurities. Sodium ethoxide, added to an alcoholic solution of nitrocamphor, was found to produce an acceleration very similar to that which results from the addition of caustic potash to an aqueous solution of glucose; the mutarotation in presence of N/1000 NaOEt was complete in about a quarter of an hour, with N/10,000 NaOEt in about three hours, and a slight acceleration could be detected in presence of N/100,000 NaOEt. The normal period of the isomeric change in absolute alcohol at 20° C. is about six hours, but the change is greatly accelerated by the addition of a little water. The velocity of change in alcohol containing 1 per cent of water was exactly equal to that in a sample of 99·8 per cent alcohol to which sodium ethoxide had been added in a concentration of N/10,000.

Extraordinary effects were produced by the addition of piperidine to solutions of nitrocamphor in benzene. In presence of N/1000 piperidine the mutarotation was complete in two minutes, and even when working as rapidly as possible only two readings of the polarimeter could be obtained before the final value was reached. With N/10,000 piperidine the change was complete in about six minutes, with N/100,000 in an hour, and with N/1,000,000 in about ten hours. With N/10,000,000 piperidine the acceleration of the isomeric change was comparable with that due to the trace of impurity normally present in the purified materials, and no definite observations could be made.

In the case of the N/100,000 solution the molecules are present in the proportion—

Piperidine : nitrocamphor : benzene = 1 : 25,000 : 1,000,000,

and about 2 per cent of the nitrocamphor undergoes change in each minute. It therefore follows that if each molecule of piperidine is able to invert only one molecule of nitrocamphor at a time, it must accomplish 500 such inversions per minute, and unless selectively guided to the nitrocamphor must come in contact also with some 20,000 molecules of benzene.

In view of the remarkable effects produced by the addition of piperidine, it is noteworthy that the addition of aniline is almost without effect. In presence of N/1000 aniline the velocity of isomeric change in a solution of nitrocamphor in benzene was slower than in presence of N/10,000,000 piperidine—a result that was confirmed by a second series of observations; the blank experiment, with benzene only, showed a still slower change, but this result was only achieved by very careful purification of the materials.

The experiments now described are of importance as indicating the conditions under which isomeric change may in general take place. It may be concluded that in neutral solvents, such as benzene and chloroform, no change can occur unless some third substance or impurity is present; the influence of the impurity may be greatly increased by raising the temperature or illuminating with ultra-violet light; but even under these conditions it is probable that isomeric change is not a spontaneous result of the interaction of solvent and solute.

The experimental evidence thus gives no support, but on the contrary is entirely opposed to the existence of the condition of intermolecular "wobble" postulated by Laar in his theory of "tautomerism" (*Ber.*, 1885, xviii., 648—657). It is, moreover, very doubtful whether even the special case of the process of "bond-shifting," or "desmotrophy" (Jacobson, *Ber.*, 1888, xxi., 2628), which does not involve the transference of a mobile hydrogen atom, and which Baly (Stewart and Baly, *Trans. Chem. Soc.*, 1906, lxxxix., 498) has described as "isorropesis," could occur in pure neutral solvents in the absence of a catalytic agent.

In addition to the investigation described above considerable attention has been paid during the past year to the study of the optical properties of dynamic isomerides, and preparations have been made for a detailed examination of the relationship between the absorption spectra of isodynamic compounds and the velocity with which they undergo isomeric change.

* Report of the Committee, consisting of Professor H. E. Armstrong (Chairman), Dr. T. M. Lowry (Secretary), Professor Sydney Young, Dr. J. J. Dobbie, Dr. A. Lapworth, Dr. M. O. Forster, and Dr. C. H. Desch. (Drawn up by the Secretary). Read before the British Association (Section B), Leicester Meeting, 1907.

THE STUDY OF HYDRO-AROMATIC SUBSTANCES.*

(Concluded from p. 79).

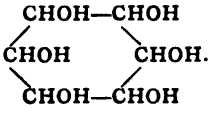
Recent Work on Hydro-aromatic Substances.
By Professor A. W. CROSSLEY.

Hydrocarbons.—The ozonides of hydro-aromatic hydrocarbons (Harries and Neresheimer, *Ber.*, 1906, xxxix., 2846) produced by the direct addition of ozone to a double bond in a six carbon ring, differ markedly from analogous derivatives obtained from open chain hydrocarbons, or from members of the aromatic series, in being very stable towards water. Thus, the ozonide of 1 : 1 : 3-trimethyl-Δ^3-tetrahydrobenzene (cyclogeraniolene) is with difficulty acted on by water; the ozonide of tetrahydrobenzene is slowly changed by boiling with water, yielding principally adipic acid and small quantities of adipic aldehyde, whereas the ozonide of dihydroxylene does not give any definite products. Furthermore, the ozonides of hydro-aromatic hydrocarbons show irregularities in their composition, for though tetrahydrobenzene ozonide has the normal composition $C_6H_{10}O_3$, the derivatives obtained from 1 : 1 : 3-trimethyl-Δ^3-tetrahydrobenzene appears to contain four atoms of oxygen and to possess a double molecular weight. This alone would not preclude the use of such substances for the determination of the constitution of hydro-aromatic hydrocarbons if they were not so difficult to decompose with water. It has, however, now been ascertained that reduction of the ozonides leads to the production of the same aldehydes or ketones as would be formed by the action of water; or, if very energetic reducing agents are employed, to the corresponding alcohols. But the method

* Report of the Committee, consisting of Dr. E. Divers (Chairman), Prof. A. W. Crossley (Secretary), Prof. W. H. Perkin, Dr. M. O. Forster, and Dr. H. R. Le Sueur. Read before the British Association (Section B), Leicester Meeting, 1907.

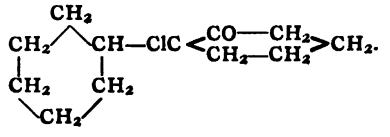
possesses the disadvantage that it is not so easy to make a quantitative estimation of the products as when the decomposition is brought about by water.

Alcohols.—Scyllite, discovered in 1856, by Staedeler in certain cartilaginous fishes, has been further examined by Müller (*Ber.*, 1907, xl., 1821). It has the formula $C_6H_{12}O_6$, forms monoclinic crystals melting in the neighbourhood of 360°, is but slightly soluble in water, is optically inactive, and gives a hexacetyl derivative. It is concluded from this evidence that scyllite is a hexahydroxyhexahydrobenzene, and is one of the inactive forms of inosite.

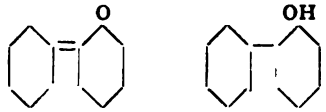


Ketones.—Ketohexahydrobenzene, like phloroglucinol and dihydroresorcin, is capable of existing in two tautomeric forms, either as the ketone or as hydroxy-Δ^1-tetrahydrobenzene, for when heated with acetic anhydride and sodium acetate (Mannich, *Ber.*, 1906, xxxix., 1594) it yields the acetyl derivative of hydroxytetrahydrobenzene. The latter is a colourless oil boiling at 180—182°, and possessing a pleasant fruity odour. It is readily oxidised by potassium permanganate, giving adipic acid, and is hydrolysed by alcoholic potassium hydroxide with regeneration of ketohexahydrobenzene.

Condensation products of a varied nature have been obtained from ketohexahydrobenzene; thus when hydrogen chloride is passed into the pure ketone (Wallach, *Ber.*, 1907, xl., 70) a solid product results, having the formula $C_{12}H_{19}OCl$, and the probable constitution—

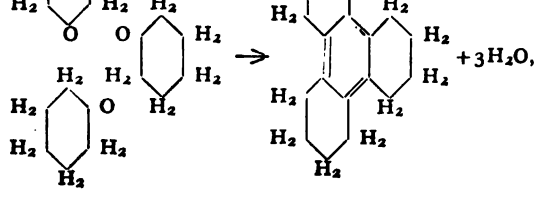


This substance loses hydrogen chloride to form cyclohexenecyclohexanone (XXI.), which on reduction gives the corresponding saturated alcohol (XXII.). From this latter body, by treatment with hydrogen iodide, the fully hydrogenised dicyclohexane or dicyclohexyl, $C_6H_{11}.C_6H_{11}$ is formed.

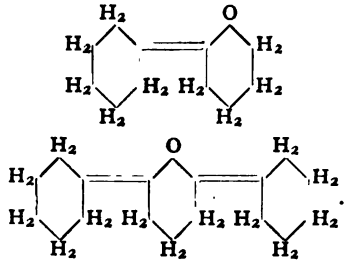


XXI. XXII.

If alcoholic sulphuric acid be used as condensing agent, then Mannich (*Ber.*, 1907, xl., 153) finds that ketohexahydrobenzene behaves similarly to acetone, yielding bodies analogous, as regards method of formation, to mesityl oxide, phorone, and mesitylene, and having the respective formulæ $C_{12}H_{18}O$, $C_{18}H_{26}O$, and $C_{18}H_{24}$. The latter would obviously be produced from three molecules of ketohexahydrobenzene, according to the following scheme:—



which shows it to contain a benzene ring and three hydrogenised benzene rings, and it would therefore be dodecahydrotriphenylene. It crystallises in compact prisms melting at 232—233°, when oxidised with fuming nitric acid yields mellitic acid, and on distillation with zinc-dust in an atmosphere of hydrogen (*Ber.*, 1907, xl., 159) is converted into triphenylene, identical with the substance previously described by Schmidt and Schultz (*Annalen*, 1880, cciii., 135). The ketones $C_{12}H_{18}O$ and $C_{18}H_{26}O$ have probably the following constitutions:—

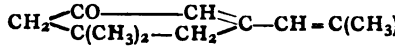


Homologues of ketohexahydrobenzene can be produced by the slow distillation of the anhydrides of substituted pimelic acids, when they lose carbon dioxide. Blanc (*Comptes Rendus*, 1907, cxliv., 143) has by this means prepared from $\beta\beta$-dimethylpimelic anhydride 3-keto-1 : 1-dimethylhexahydrobenzene (see *ante*), which when reduced with sodium and absolute alcohol gives 3-hydroxy-1 : 1-dimethylhexahydrobenzene, identical in every respect with the product obtained by Crossley and Renouf (see *ante*) by the reduction of chloroketodimethyltetrahydrobenzene. 3-Keto-1 : 1 : 4-trimethylhexahydrobenzene has been prepared by a similar reaction.

1 : 2-, 1 : 3-, and 1 : 4-ketomethylhexahydrobenzenes (Wallach, *Annalen*, 1906, cccxlvi., 249).

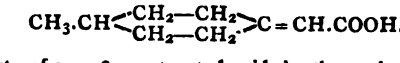
2-Chloro-1-ketohexahydrobenzene is obtained by treating ketohexahydrobenzene suspended in water with chlorine in presence of calcium carbonate (Bouveault and Chereau, *Comptes Rendus*, 1906, cxlii., 1086). When boiled with a strong solution of potassium carbonate it is converted into 2-hydroxy-1-ketohexahydrobenzene, and when treated by Grignard's reaction yields ketomethyl-(ethyl, &c.)-hexahydrobenzene.

A compound isomeric with Pinner's xylitone is formed by the action of sodium ethoxide on a mixture of ethyl acetoacetate and phorone (Knoevenagel and Schwartz, *Ber.*, 1906, xxxix., 3441), and is supposed to be 1-keto-3-isobutenyl-5 : 5-dimethyl-Δ^3-tetrahydrobenzene. It yields

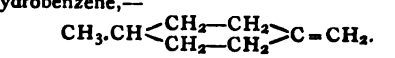


a tetrabromide, and when reduced with sodium and alcohol gives 1-hydroxy-3-isobutyl-5 : 5-dimethylhexahydrobenzene, which under the influence of phosphorus pentoxide loses water to form 3-isobutenyl-5 : 5-dimethyl-Δ^1-tetrahydrobenzene.

Acids.—Marckwald and Meth (*Ber.*, 1906, xxxix., 2035) have further investigated 1-methylcyclohexylideneacetic acid, to which allusion was made in the last report. (*Reports*, 1906, p. 264). This acid shows the general



property of an $\alpha\beta$-unsaturated acid, in that, when heated, it readily loses the elements of carbon dioxide to give a hydrocarbon, C_8H_{14}, which is optically inactive, and has already been proved by Wallach to be 1-methyl-4-ethylenehexahydrobenzene,—



Further, as is well known, the bromo-additive compounds of $\alpha\beta$-unsaturated acids readily lose carbon dioxide

and hydrogen bromide to give brominated hydrocarbons :—

$$R.CHBr.CHBr.COOH \rightarrow R.CH{:}CHBr.$$

Methylcyclohexylideneacetic acid behaves in a similar way (Marckwald and Meth, *Ber.*, 1906, xxxix., 2404), for when treated with bromine in aqueous sodium carbonate solution it is converted into 1-methyl-4-bromomethylene-hexahydrobenzene, which on heating with water forms

$$CH_3.CH<\begin{matrix}CH_2—CH_2\\CH_2—CH_2\end{matrix}>C=CHBr.$$

hexahydro-*p*-tolualdehyde. Perkin and Pope (*Proc. Chem. Soc.*, xxii., 107) prepared their methylcyclohexylidene-acetic acid by eliminating the elements of hydrogen bromide from α-bromohexahydro-*p*-tolylacetic acid, and, as

$$CH_3.CH<\begin{matrix}CH_2—CH_2\\CH_2—CH_2\end{matrix}>CH—CHBr—COOH.$$

shown by Ruppe, Roners, and Lotz (*Ber.*, 1902, xxxv., 265), both αβ- and βγ-unsaturated acids are formed by loss of hydrogen bromide from α-bromo acids. Marckwald and Meth suggest that Perkin and Pope's acid is 1-methyl-Δ^6-tetrahydrobenzeneacetic acid, and that the methylcyclo-

$$CH_3.CH<\begin{matrix}CH_2—CH\\CH_2—CH_2\end{matrix}>C.CH_2.COOH.$$

hexylideneacetic acid, which would be produced at the same time, was overlooked on account of its extreme solubility in all organic solvents.

m-Hydroxybenzoic acid can be readily reduced by sodium and alcohol (Perkin and Tattersall, *Journ. Chem. Soc.*, 1907, xci., 480) to form cyclohexanol-3-carboxylic

$$CH_2<\begin{matrix}CHOH—CH_2\\CH_2——CH_2\end{matrix}>CH.COOH.$$

acid, which exists in well-defined *cis*- and *trans*-modifications. When oxidised with chromic acid it is converted into cyclohexanone-3-carboxylic acid, the ethyl salt of which has been used as the starting-point in the synthetical preparation of carvestrene. The method of preparing δ-ketohexahydrobenzoic acid from pentane-αγε-tricarboxylic acid is very laborious, and a decided improvement has now been introduced (Kay and Perkin, *Ibid.*, 1906, lxxxix., 1640) by heating the ethyl ester of the above acid with sodium, when ethyl cyclohexanone-2 : 4-dicarboxylate is formed, which, when digested with dilute

$$C_2H_5COO.CH<\begin{matrix}CH_2.CH_2.COOC_2H_5\\CH_2.CH_2.COOC_2H_5\end{matrix}\rightarrow$$

$$\rightarrow C_2H_5.OOC.CH<\begin{matrix}CH_2—CH_2\\CH_2—CH_2\end{matrix}>CO\ .\ COOC_2H_5$$

sulphuric acid, is readily decomposed with formation of δ-ketohexahydrobenzoic acid, carbon dioxide, and ethyl alcohol.

Confirmation of the formulæ assigned by Baeyer (*Annalen*, 1892, cclxix., 145) to the different forms of dihydrophthalic acids has been furnished through the resolution of *trans*-Δ3 : 5-dihydrophthalic acid (Neville, *Journ. Chem. Soc.*, 1906, lxxxix., 1744) into two active isomerides by crystallising the strychnine hydrogen salt, the isomerides having $[\alpha]_D$ 126°. Baeyer stated that when treated with caustic soda the *trans*-Δ3 : 5 acid was converted into the Δ2 : 6 variety ; and with acetic anhydride it passed the *cis* Δ3 : 5 modification. As neither of these forms contains an asymmetric carbon atom the optical activity ought to be destroyed by treatment with these reagents. This takes place in both cases, the change from one modification to the other proving to be a unimolecular reaction under the conditions of experiment.

A comparison of the electrical conductivities of α- and β-naphthoic, benzoic, and phthalic acids with their hydrogenised derivatives leads Abati (*Cent. Blatt.*, 1907, i., 886) to the conclusion that, apart from the strongly negative character of the aromatic nucleus, the presence and position of double bonds in these acids has an undoubted influence on their conductivities, which is increased by a double bond in the αα- or βγ-positions, whereas if in the αβ- or γδ-positions practically the same value is obtained as for the corresponding saturated acids. The author considers this to be contrary to the declarations of Fichter and Pfister (*Annalen*, 1904, cccxxxiv., 201), and does not consider that constitutional formulæ should be assigned from the results of single reactions, as has been done by Perkin and Pickles (*Journ. Chem. Soc.*, 1905, lxxxvii., 293) in the case of the tetrahydroisophthalic acids. Abati and Minerva (*Cent. Blatt.*, 1907, i., 887) have isolated hydrophthalic acids by the reduction of phthalic acid with sodium amalgam, and give the principal properties of these acids and their anhydrides.

Steric Hindrance in the Formation of Rings.—The interaction of the 1 : 4-dibromides and primary aromatic amines has been previously shown by Scholtz (*Ber.*, 1898, xxxi., 414, 627, 1154, 1707 ; and 1899, xxxii., 848) to take place in one or two ways, according as to whether the primary amine contains a substituting group in the ortho-position or not. Thus, with *o*-xylylene dibromide and aniline or *m*- and *p*-toluidine a five-ring compound is formed :—

$$C_6H_4<\begin{matrix}CH_2Br\\CH_2Br\end{matrix}+H_2N.C_6H_5=$$

$$=C_6H_4<\begin{matrix}CH_2\\CH_2\end{matrix}>N.C_6H_5+2HBr\ ;$$

whereas when *o*-toluidine is used an open chain substance results :—

$$C_6H_4<\begin{matrix}CH_2Br\\CH_2Br\end{matrix}+2H_2N.C_6H_4.CH_3=$$

$$=C_6H_4<\begin{matrix}CH_2.NH.C_6H_4.CH_3\\CH_2.NH.C_6H_4.CH_3\end{matrix}+2HBr.$$

The reaction has now been extended to the formation of six-ring systems (Scholtz, *Ber.*, 1907, xl., 852), where the condensation of numerous substances has shown that exactly similar conditions hold good ; for *o*-toluidine condenses with pentamethylene dibromide to give pentamethylene-di-*o*-toluidine, $(CH_2)_5.(NH.C_6H_4.CH_3)_2$, whereas with *m*- or *p*-toluidine there is formed *m*- or *p*-tolylpiperidine.

$$CH_2<\begin{matrix}CH_2—CH_2\\CH_2—CH_2\end{matrix}>N.C_6H_4.CH_3.$$

Optical Influence of Conjugated Unsaturated Groups.—Kay and Perkin (*Journ. Chem. Soc.*, 1906, lxxxix., 839) have shown that the magnetic rotation of *d*-limonene differs from that of Δ3,8(9)-*p*-menthadiene, of which the value is abnormally high, and they expressed the belief that this was due to the presence of two conjugated double bonds. Bruhl (*Journ. Chem. Soc.*, 1907, xci., 115 ; see also *Ber.*, 1907, xl., 878) points out that this is correct, and that the high value could have been predicted with certainty, for Bruhl's previous work has proved that the numbers for the magnetic rotations and refractive values of substances are always largely increased by the presence of conjugated double linkings, not only C:C.C:C but also C:C.C:O. Only benzene derivatives, which contain monovalent atoms or groups substituting hydrogen atoms of the ring, give normal values, and here it is presumed that the three double bonds mutually neutralise one another. As soon as the symmetry of the six carbon atoms is disturbed by the introduction of CH_2 between the members of the ring, or by coupling the ring with other unsaturated groups, such as C:C, C:O, NO_2, &c., then the characteristic increase in value due to the conjugated bonds is shown.

Velocity of Chemical Change in the Polymethylene Series.—The following may be quoted as some of the more important general results of the study of polymethylene derivatives in respect to the velocity of chemical change (Menschutkin, *Journ. Chem. Soc.*, 1906, lxxxix., 1532).

The formation of the closed polymethylene ring from an open chain of normal structure proceeds with increase of velocity, the maximum occurring in the formation of

the pentamethylene ring, decreasing through the hexamethylene, to the minimum increase in the case of the heptamethylene ring. The increase of velocity at the closing of the open chain is not a specific property of the polymethylene ring, but is observed in the formation of all rings, alicyclic and heterocyclic. The secondary polymethylene alcohols, in which the hydroxyl group is attached to the carbon atom of the ring, are typical secondary alcohols. Their esterification constants are higher than those of the normal saturated secondary alcohols; derivatives of cyclopentanol giving the highest, cyclohexanol much lower, and cycloheptanol the lowest values. The esterification constants of polymethylene tertiary alcohols are very low, but esterification proceeds regularly. This is characteristic of phenols, and does not occur with saturated tertiary alcohols. When side chains are present in the ortho- or diortho-positions a great decrease in the esterification constants is observed, an effect commonly ascribed to the benzene ring alone, but in reality a general property of all chains. Side chains in positions 3 or 4 of the polymethylene series produce an increase of the constants; and as open chain compounds show no such increase of velocity this provides an important characteristic of closed chains. When a hexamethylene ring is introduced into the open chain of an alcohol the decrease of the esterification constants is much larger than is effected by the benzene ring.

ON THE NATURE OF VALENCY.*

By Prof. W. J. POPE and W. BARLOW.

(Concluded from p. 82).

From the cases here briefly described, which with others have been discussed in detail elsewhere (*Trans. Chem. Soc.*, 1907, xci., 1150), it is concluded that the crystal structures of compounds composed of two or more elements of the same valency are to be regarded as close-packed homogeneous assemblages of spheres; atoms of the different component elements are to be represented in the assemblage by different kinds of spheres, and all are nearly, but not precisely, of the same volume. The assemblage of spheres is to be regarded as subject to pressure for the purpose of eliminating interstitial space, and so causing the assemblage to simulate an equilibrium between centres of attraction and repulsion. An indication is thus obtained that in the substances concerned the volume appropriated by each atom is approximately proportional to its valency; it is also clear that crystalline substances are, in general, capable of formulation as close-packed assemblages of spheres, each of which represents the sphere of influence of a component atom. On considering the properties of close-packed homogeneous assemblages of spheres of different sizes, the assemblages being supposed subject to the previously mentioned condition as to compression, two are found which are of special importance. These are termed the first and second geometrical properties of homogeneous close-packed assemblages of spheres, and may be stated in the following terms:—

First Geometrical Property.—Let homogeneously situated spheres, each of volume m, be removed from a homogeneous, close-packed assemblage of deformable spheres, and let the similar vacant spaces disclosed be reoccupied each by a similar group consisting of two or more spheres having the total volume m: then if the shape of the cavities can, without re-marshalling the assemblage, be adjusted to the shape of the introduced groups by some mere distortion and local adjustment, the close-packing is found to be preserved.

Second Geometrical Property.—If the molecular units of two homogeneous assemblages of deformable spheres, which are about equally closely packed, are partially similar in composition, and the similar parts have the same marshalling in both, whilst the dissimilar parts are of different valency volumes, the amount of the difference will be two volumes, or a simple multiple, 2, 3, or 4, of two volumes of the sphere of influence of minimum magnitude, namely, corresponding to valency 1, for every molecular unit.

The first geometrical property is entirely analogous to that aspect of the doctrine of valency which says that one set of atoms of the total valency m is chemically replaceable by another set of atoms of the total valency m. The second geometrical property is entirely analogous to that aspect of chemical substitution which states that if an atom of valency m is replaced by one of valency $m+n$, other atoms of the total valency n must also be introduced in order that the type of the original molecular structure may be preserved; it also shows why a multivalent element in general changes its valency by 2 or by integral multiples of 2 units. This close analogy between the indications of the doctrine of valency and the properties of close-packed assemblages of spheres is put forward as having a physical meaning, and leads to the conclusion that in a crystalline substance each component atom appropriates a portion of space which is approximately proportional in volume to its fundamental valency. The fundamental valency of an element must thus be regarded as of a different nature from other valencies exhibited by the same element, just as has been indicated by the work of Werner and Abegg, and it has not thus far been found necessary to suppose that multivalent elements affect, under different conditions of combination, spheres of influence of different sizes corresponding to the several valencies. The sphere of influence of nitrogen is of approximately three times the volume of that of hydrogen both in ammonia and ammonium chloride, and that of sulphur is approximately twice as large as that of hydrogen in compounds in which this element is di-, tetra-, or hexavalent.

It should be observed that the relation noted between the volumes of the spheres of influence and the valencies of the element is to be expected to hold in all compounds, each taken alone, but that it does not necessarily hold as between one compound and another, or between different physical states of any one compound. As above indicated, the relative and not the absolute volumes are alone concerned in the present work. If the above view of the nature of crystalline substances is correct, each crystalline substance must be regarded as a close-packed homogeneous assemblage of the spheres of atomic influence, and the chemical molecule must be regarded as the contents of the cell produced by an appropriate homogeneous geometrical partitioning of the assemblage into clusters of spheres. Much evidence of the correctness of this mode of formulation has been quoted above and more may be now conveniently given.

If, in a series of related substances, the axial ratios are so chosen, either by accident or design, as to refer to the relative dimensions of similar parts of the crystal structure in the several cases, the equivalence parameters should at once reveal the relation between the substances. This is seen in the case of the humite group of minerals, which consists of the monosymmetric chondrodite, $Mg_3(SiO_4)_2,2Mg(F,OH)$; the orthorhombic humite, $Mg_5(SiO_4)_3,2Mg(F,OH)$; and the monosymmetric clinohumite, $Mg_7(SiO_4)_4,2Mg(F,OH)$; the axial ratios and equivalence parameters of these substances are given in Table A. The practical constancy of the values x, y, and z/W (W being the sum of the valencies or the valency volume) indicates that the increment of the series, Mg_2SiO_4, is introduced as a succession of layers which lie parallel to the directions a and b and perpendicular to the direction c. The increment of composition in the series is Mg_2SiO_4, the composition of the orthorhombic forsterite, and by subtracting the increment from the composition of chondrodite the residue, $MgSiO_4,2Mg(F,OH)$,

* Paper forming the basis of a Discussion on this subject at the Leicester Meeting of the British Association (Section B), 1907.

TABLE A.

	W.	a : b : c	x : y : z	z/W.
Chondrodite	38	1·08630 : 1 : 3·14472	2·4249 : 2·2323 : 7·0199	0·18473
Humite	54	1·08021 : 1 : 4·40334	2·4278 : 2·2475 : 9·8965	0·18327
Clinohumite	70	1·08028 : 1 : 5·65883	2·4349 : 2·2540 : 12·7547	0·18221
Prolectite { Observed ..	22	1·0803 : 1 : 1·8862	2·3877 : 2·2102 : 4·1689	
Prolectite { Calculated ..		1·0822 : 1 : 1·8500	2·4292 : 2·2446 : 4·1526	
Forsterite { Observed ..	16	0·9296 : 1 : 1·1714	2·4492 : 2·2769 : 2·8691	
Forsterite { Calculated ..		0·9240 : 1 : 1·1804	2·4292 : 2·2446 : 2·8674	

TABLE B.

d-$C_{10}H_{14}O_3$	60	1·0011 : 1 : 1·7270	3·2655 : 3·2618 : 5·6331	
d-$C_{10}H_{16}O_4$,$\frac{1}{2}(CH_3)_2CO$ ..	74	1·2386 : 1 : 1·7172	4·0435 : 3·2646 : 5·6060	

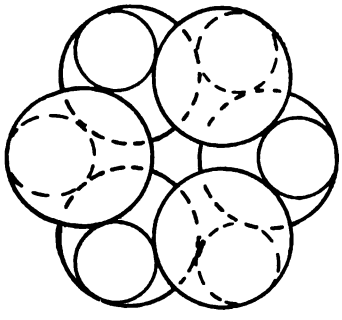


FIG. 6*a*.

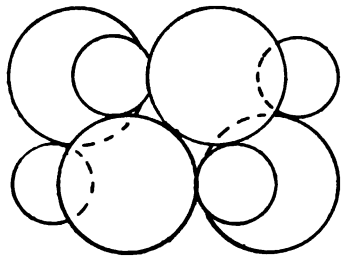


FIG. 6*b*.

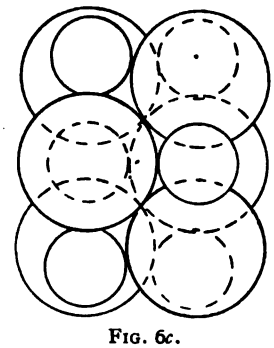


FIG. 6*c*.

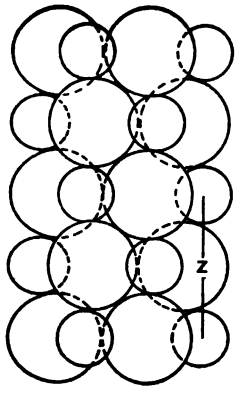


FIG. 7.

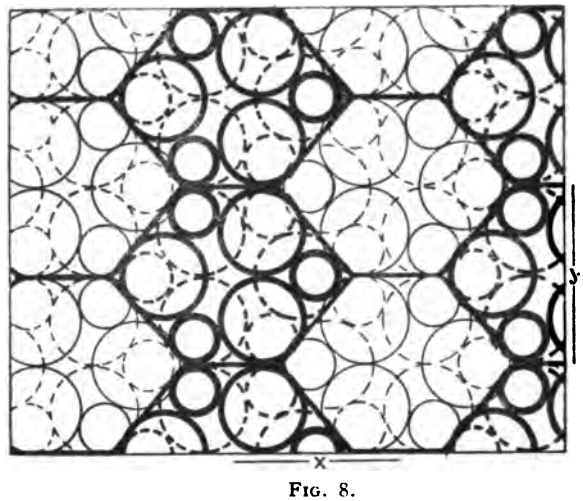


FIG. 8.

is obtained; this is the composition attributed to the monosymmetric prolectite. The equivalence parameters and the axial ratios for the two last-named minerals should be deducible from the data given for the first three; the values thus calculated and those actually observed are given in Table A.

The dimensions of the increment layer agree closely with those of the mineral forsterite, and a similar close agreement is found between the calculated and observed dimensions of the layer which may be regarded as the foundation of the series and has the composition of prolectite.

Another interesting case of similar character is furnished by the comparison of the two orthorhombic compounds, *d*-camphoric anhydride and the addition compound of *d*-camphoric acid with acetone, data for which are given in Table B.

The fact that the passage from the simpler to the more complex compound is accompanied by an increase of one of the three equivalence parameters, whilst the other two remain practically unchanged, is again indicative of the relation which the analogy suggests as existing between the relative molecular dimensions and the valency of the constituent atoms.

The first geometrical property would appear to be responsible for the close morphotropic relationships observed between the members of each of the following pairs of substances:—

1. Ammonium iodate and ammonium fluoriodate, NH_4IO_3 and $NH_4IF_2O_3$.
2. The stable and labile *o*-sulphobenzoic chlorides,—

$$C_6H_4<\begin{matrix}SO_2Cl\\COCl\end{matrix} \text{ and } C_6H_4<\begin{matrix}SO_2\\CCl_2\end{matrix}>O.$$

3. Phthalic and *o*-sulphobenzoic acid,—

$$C_6H_4(CO.OH)_2 \text{ and } C_6H_4\begin{matrix}CO.OH\\SO_2.OH\end{matrix}.$$

4. Benzoic acid and benzenesulphonic acid, $C_6H_5.CO_2H$ and $C_6H_5.SO_3H$.
5. Sulphoacetic and methionic acids,—

$$CH_2\begin{matrix}CO.OH\\SO_2.OH\end{matrix} \text{ and } CH_2(SO_2.OH)_2.$$

The second geometrical property may be regarded as responsible for the close crystallographic relationship observed between the rhombohedral sodium nitrate and calcite, the orthorhombic potassium nitrate and aragonite, the alkali salts of methanedisulphonic acid, $CH_2(SO_3H)_2$, and iminodisulphonic acid, $NH(SO_3H)_2$, and between benzene, aniline hydrobromide, and aniline nitrate (*Trans. Chem. Soc.*, 1906, 1732).

Since the publication of the conclusions here described as to the nature of valency important corroborative evidence has been put forward by Le Bas (*Trans. Chem. Soc.*, 1907, 112) and by Traube (*Berichte*, 1907, xl., 130, 723). Le Bas shows that the molecular volumes of the normal paraffinoid hydrocarbons determined in the liquid state at the melting point, and hence under practically corresponding conditions, can be calculated with great accuracy as the product of the sum of the valencies, or the valency volume W, and a unit stere S, having the value 2·970. The latter value represents the volume appropriated by a hydrogen atom in each of the liquid substances, and is one-fourth of the volume appropriated by a carbon atom throughout the series of compounds. The kind of correspondence which holds between the observed and calculated values is conveniently illustrated by the following table, given by Le Bas:—

Saturated Normal Paraffins.

	W.	Mol. vol. =V.	M.p./b.p.	V/W=S.	W×S= calculated mol. vol.
$C_{11}H_{24}$ ..	68	201·4	0·527	2·962	201·96
$C_{12}H_{26}$ ..	74	219·9	0·536	2·971	219·78
$C_{13}H_{28}$ ..	80	237·3	0·524	2·966	237·60
$C_{14}H_{30}$ ..	86	255·4	0·530	2·970	255·42
$C_{15}H_{32}$ ..	92	273·2	0·520	2·970	273·24
$C_{16}H_{34}$ ..	98	291·2	0·519	2·971	291·06
$C_{17}H_{36}$ ..	104	309·0	0·513	2·971	308·88
$C_{18}H_{38}$ ..	110	326·9	0·512	2·971	326·70
$C_{19}H_{40}$ ..	116	344·7	0·506	2·971	344·52
$C_{20}H_{42}$ ..	122	362·5		2·971	362·34
$C_{21}H_{44}$ ..	128	380·3		2·971	380·16
$C_{22}H_{46}$ ..	134	398·3		2·972	398·00
$C_{23}H_{48}$ ..	140	416·2		2·971	415·80
$C_{24}H_{50}$ ..	146	434·1		2·973	433·62
$C_{27}H_{56}$ ..	164	487·4		2·972	487·08
$C_{31}H_{64}$ ..	188	558·4		2·970	558·36
$C_{32}H_{66}$ ..	194	576·2		2·970	576·18
$C_{35}H_{72}$ ..	212	629·5		2·969	629·64

Mean value of S = 2·970.

Similar results have been obtained by Traube with molecular volumes and molecular refractions; they indicate that in the particular cases discussed the spheres of influence of the component elements remain of the same volumes throughout the series under corresponding conditions. Barlow and Pope indicated that the spheres of influence are approximately proportional in volume to the valencies in one and the same compound, and did not suggest that in general the sphere of influence of a particular element would preserve its volume on passing from compound to compound. It should of course be possible to compare series of substances under temperatures and pressures at which the relation indicated by Le Bas holds, and, in the case of the normal paraffins, it appears that these temperatures are the corresponding temperatures.

Accepting the conclusion that crystalline substances are to be regarded as homogeneous close-packed assemblages of spheres of atomic influence, the latter having volumes approximately proportional to the valencies of the corresponding elements, it is possible to deduce configurations for organic substances of considerable molecular complexity. Applying the method described above to the case of benzene, with the aid of the known crystalline form and the chemical properties of the hydrocarbon, an assemblage representing benzene can be derived, and this, by appropriate geometrical partitioning, can be divided into cells each containing one chemical molecule. The molecular configuration of benzene thus derived is shown in plan and two elevations in Fig. 6, *a*, *b*, and *c*; these molecular groups are arranged in columns as shown in Fig. 7, and these columns are packed in the crystalline assemblage in the manner indicated in plan in Fig. 8. In the assemblage the columns are arranged in walls, and the latter are packed together on two different levels, as shown by the lightly and heavily marked circles in Fig. 8. The nature of the partitioning which divides the assemblage into cells each containing one complex, C_6H_6, is indicated by the heavily marked hexagonal outlines shown in the diagram. The equivalence parameters, $x : y : z = 3·101 : 3·480 : 2·780$, calculated from the axial ratios, $a : b : c = 0·891 : 1 : 0·799$, of the orthorhombic crystalline hydrocarbon are indicated in the diagrams. The configuration thus derived represents the facts involved in the isomerism of, and the absence of enantiomorphism in, benzene derivatives; it also indicates a difference in kind between the meta-position as compared with the ortho- and para- positions (*Trans. Chem. Soc.*, 1906, 1692).

In addition to the results briefly described in the foregoing pages and which have already been published, it has been found that assemblages representative of all the paraffins, the olefines, and acetylenic hydrocarbons can be devised, and that these exhibit properties corresponding to those of the various substances. It has also been found that in the cases of tautomeric substances alternative methods of partitioning the assemblage are possible, and that these different modes of partitioning lead to the production of molecular units corresponding in constitution to the several tautomeric or dynamically isomeric modifications.

AN ELECTRICAL EXPERIMENT FOR ILLUSTRATING THE TWO MODES OF CONDENSATION OF MOISTURE ON SOLID SURFACES.

By Prof. FRED. T. TROUTON, F.R.S.

EXPERIMENT has shown what might perhaps have been anticipated from theoretical considerations, that there are two possible modes in which condensed water vapour on solid surfaces can exist and be in equilibrium with a given vapour pressure.

After which of these modes condensation will take place on bringing a surface into a moist atmosphere depends on its previous history. If the surface has been dried at a high temperature with the aid of phosphorus pentoxide the amount of moisture is relatively small, and is said to be of the *a* type, but if the drying has been effected at only ordinary temperatures there is considerably greater condensation, called the *b* type. This is attributed to there being in the latter case still some of the liquid on the surface, affording an example or nucleus for liquid condensation of the *b* type; while in the former case the condensation is more analogous to the supersaturated state which can occur when a vapour is compressed along an isothermal in the absence of the nuclei necessary for condensation.

When a completely dried surface of glass is placed in an atmosphere of which the moisture is gradually increased

* A Paper read before the British Association (Section A), Leicester Meeting, 1907.

up from zero, the course of events is as follows :—At first very little moisture condenses compared to that which takes place if the drying has been incomplete, but on reaching a certain critical vapour pressure the condensation is very rapid, and is now of the *b* type.

The electrical conductivity of these two types of condensed surface layers is very different. A comparative experiment was made in which two rods of glass were laid from earth to the knobs of two electroscopes passed up for the purpose into a vessel in which the percentage of moisture could be changed at will. One of these rods was dried by heating, while the other was not. As the percentage of moisture was increased, the air-dried rod was observed to gradually acquire considerable conducting powers, but the other rod did not conduct until the critical pressure was reached, when it did so suddenly. The critical pressure for glass is roughly 50 per cent saturation, the same as that found by the deposition method described above.

In the case of shellac the critical pressure was found to be above 90 per cent. A simple experiment illustrating the two modes of condensation was exhibited. An electroscope with shellac insulation was covered by a bell-jar which had previously been held for a moment over a Bunsen flame, so as to acquire a damp atmosphere. No discharge occurred. The experiment was now repeated, but the shellac was first moistened, and then dried with a cloth so as to again insulate. On the electroscope being covered by the bell-jar immediate discharge took place, even though, in the meantime, the air in the jar must have somewhat dried; this was of the *b* or conducting type of condensation.

On now melting the surface of the shellac so as to completely dry it, the surface was found to have reverted to the condition in which the *a* type of condensation is deposited.

THE ABSORPTION OF GASES BY CHARCOAL.*

By Miss IDA F. HOMFRAY.

THE experiments of which an account is here submitted were devised, at the suggestion of Sir William Ramsay, to throw some light on the question of the absorption of gases in charcoal. The gas which appeared most suitable for the purpose, on account of its molecular simplicity and chemical inertness, was argon. The apparatus used was similar to a constant-volume gas thermometer, the bulb containing 3 grms. of charcoal. This was connected with a gas burette, a gas reservoir, and a Sprengel pump, all connections being of glass and sealed.

Various constant temperature baths were used, ranging from boiling water to liquid-air temperatures, and successive quantities of argon were admitted from the burette, the pressures being read at each temperature. Isothermal curves were then plotted, taking pressures as ordinates and concentrations (corrected for dead space and reduced to standard conditions) as abscissæ. From these curves points of equal concentration were read off and a fresh series of curves were obtained, having pressures as ordinates and absolute temperatures as abscissæ. Such curves have been termed by Ostwald "isosteres." Each curve corresponds thus to a vapour-pressure curve in the univariant system of a vapour in contact with its own liquid, and is analogous to it in form.

Ramsay and Young's law for the ratios of the absolute temperatures of two vapours at the same pressure was then applied to these results in the form :—

$$\frac{T_0}{T_1} - \frac{T_0'}{T_1'} = K(T_0 - T_0');$$

where T_1 T_1' are the absolute temperatures read from one of the isosteric curves corresponding to any two pressures, and T_0 T_0' the absolute temperatures of any other vapour, taken as standard, at the same two pressures. Water, oxygen, and argon were successively taken as standards, and the equation was found to hold in all cases. A series of straight lines, one for each concentration, was thus obtained.

It has been shown by Professor Porter that Ramsay and Young's law may be directly derived from Bertrand's vapour-pressure formula,—

$$P = G\left(\frac{T-a}{T}\right)^n,$$

provided that the constant n is the same for all vapours. For a large range of vapours it is found that if $n = 50$ very good correspondence is obtained. This was found also to be the case with the results of the present experiments.

Values of the other constants a and g were calculated for each concentration as well as for argon vapour itself.

An attempt has been made to correlate these constants with numbers representing the actual concentrations, and, in order to introduce the argon-vapour constants at a finite concentration, the concentrations were calculated in terms of weight of argon in 100 grms. of the mixture—a method frequently used in the case of solutions. The concentrations experimentally reached varied from 0·317 to 7·089 per cent, the vapour in the absence of charcoal being represented by 100 per cent.

For convenience the logarithms of the concentrations were plotted against values of a and G respectively, and a smooth curve was obtained terminating at 100 per cent in the constants for argon.

Equations were then obtained which express with considerable accuracy these curves, and when introduced into Bertrand's equation, the corresponding temperatures or pressures calculated for any concentration are in very fair agreement with those experimentally found, except for exceedingly small concentrations.

These equations are—

$$a = 13{\cdot}12 + \frac{250}{24}\left\{\log\frac{100}{C}\right\}$$

$$\log g = 0{\cdot}1085 - 0{\cdot}012\left\{\log\frac{100}{C+1}\right\}$$

where $g = (G)\frac{\lambda}{b}$.

The values 13·12 and 0·1085 are the values respectively of a and log g for argon vapour. The equations given in this paper are in much better agreement with observation than the logarithmic or exponential equations usually employed to express the isotherms.

* A Paper read before the British Association (Section A), Leicester Meeting, 1907.

Structural Stability of Ethylene Oxide.—Louis Henry.—Grignard states that the reaction of the organo-magnesium compounds on ethylene oxide, $\overset{CH_2}{\underset{O}{\diagdown\!\diagup}}\!\overset{CH_2}{}$, gives rise to primary alcohols, but the author considered that this statement was open to doubt, because ethylene iodo-hydrine, $(HO)CH_2—CH_2I$, with organo-zinc compounds gives secondary alcohols, and, moreover, isobutylene oxide with magnesium methyl bromide gives secondary isoamyl alcohol, $(CH_3)_2=CH.CH(OH)—CH_3$. Since isobutylene oxide reacts in the same way as its isomer isobutyric aldehyde with magnesium methyl bromide, and since ethyl glycol, $(HO)CH_2—CH_2(OH)$, gives acetic aldehyde, $CH_3—CH=O$, under the same conditions as isobutyl glycol gives isobutyric aldehyde, it was to be expected that ethylene oxide (of which isobutylene oxide is the dimethyl derivative) would give rise to the aldehyde $CH_3—CH=O$, *i.e.*, to secondary alcohols. But secondary alcohols are not formed, and thus ethylene oxide does not behave like its dimethyl derivative. This fact is a remarkable example of the stability which excess of hydrogen communicates to residues and molecules containing carbon; thus hydrogen may be regarded as the cementing factor.—*Comptes Rendus*, cxlv., No. 3.

THE CONSTITUTION OF THE ATOM.*

Discussion.

The debate was opened by Prof. E. Rutherford, F.R.S., who gave a brief historical sketch of existing knowledge regarding the constitution of the atom. He said that the fundamental idea dated from the time of Dalton, but that at the present day the chemist did not regard the atom as the smallest possible particle of matter. For the last ten years physical researches had afforded experimental proofs of the atomic theory, and so far as it existed as a working chemical theory recent knowledge had not undermined it but had materially strengthened it. Coming down to purely physical work, he said that the electron must be looked upon as a sphere of electricity or as an electrified sphere. Its diameter was known to be of the order of 10^{-13} cm., and its sphere of action 10^{-12} cm. He was sure that the electron had come to stay, and that it was a constituent of all matter. Nevertheless, the stability of the atom of matter was not affected by the liberation of one or more electrons. He then referred to Lord Kelvin's idea of a number of electrons being contained by a sphere of positive electrification, and to Prof. J. J. Thomson's idea of a similar arrangement, practically the only difference being that Thomson's electrons were revolving in rings, whereas Kelvin's were stationary. He was convinced that hydrogen played a most important part in electrical conduction, and dealt further with the question of an electron being tacked on to each hydrogen atom. So far as he himself was concerned, he believed in the existence of a positive electron, and he described briefly the work of a German *savant* who claimed to have discovered positive electrons. He thought it had not been isolated hitherto simply because everybody expected that it would have properties exactly opposite to those of the negative electron, or, in other words, that it would be the mirror image of the negative electron. It might, on the contrary, have entirely different properties, and so elude the vigilance of those who were seeking it. With regard to spectrum analysis, he was of the opinion that it would not be of very great use in the investigation of the constitution of the atom. The spectrum of an element was probably not due to the element at all, but to the superficially attached electrons. Thus it might happen—and he inclined to the opinion that it did—that the spectrum due to the internal electrons of an atom—*i.e.*, to the element itself—existed only in the ultra-violet part of the spectrum and had never yet been observed. This would account for the variation of the so-called spectrum of an element with temperature. There was evidence for the radio-active point of view which showed that electrons in atoms were in violent motion, as otherwise they could not be expelled with the velocity of light.

The next speaker in the discussion was Sir Oliver Lodge, who at once avowed himself as the champion of the electric theory of matter. At all events he claimed that it was a splendid working hypothesis. He knew that everybody was not of this opinion, and Lord Kelvin himself did not hold it. In this connection he recognised that it was hazardous and interesting—painfully interesting—to differ from Lord Kelvin. He maintained the electric theory, because in whatever direction it was applied it did not break down, and if it did not break down, then it was good enough until something better turned up. The inertia of matter, for instance, could be explained electrically, because when an electric charge was in motion it set up an electric field, and an exercise of force was required to stop or retard it. Radiation could also be explained, for, when an electric charge was accelerated, it radiated in the proper direction—that is to say, it imparted vibrations to the surrounding ether. With regard to instability, if the atom were considered as a revolving assemblage, then the corpuscles experienced a centripedal acceleration and radiated, whence instability was set up. He agreed with Prof. Rutherford that the difficulty of the whole matter lay in the positive charge, of the existence of which there was no evidence whatever.

Sir Wm. Ramsay, who rose next, said that from the chemist's point of view the interest lay in the satellites or detachable electrons, and not in the internal or constitutional electrons of the atoms. Hydrogen was not an element at all, but a compound of hydrogen and electrons. Chemists wrote H – to represent an atom of hydrogen, and H – H to represent a molecule, but he was not sure whether they ought not to write H – · H. In the same way, having regard to the electrons present, an atom of what was called hydrogen ought to be written H E, where E stood for an electron. When, however, they considered a molecule of so-called hydrogen, the question arose as to whether they should write it H E H E or H E E H. For himself, he thought the former way was correct. With regard to Prof. Rutherford's statement that loss of electrons had no effect upon an element, he would like to state that, although that might be true, he had distinct evidence that increase of electrons made a difference. For instance, some time ago he sealed up some radium in a glass bulb through which only the β-rays, or electrons, could pass. In proximity to this bulb he placed a number of elements, among which was nickel. This nickel, after being bombarded with electrons, proved to be coated with a radio-active skin, and precipitated as strongly radio-active substance in sulphuric acid.

Mr. F. Soddy expressed the opinion that the time had not yet come to believe in the electric theory of matter. Indeed, all the results of the last twenty-five years of research could be accepted without applying the electric theory of the constitution of matter. He ventured to say that none of the actual experimental results arrived at by chemists concerning this subject had been predicted by physicists. The "predictions" had been applied after the experimental results had been obtained. He could not accept the theory that the loss of energy by an atom produced a change in the matter of which that atom was constituted; at all events, this drain of energy produced no effect such as might be observed by chemists. He was convinced that the ultimate solution of these problems would come from the chemists.

Mr. G. A. Schott said that the new hypothesis of each hydrogen atom having only one electron was unworkable. On this basis there were not sufficient surface electrons to the atom to account for the number of lines in the spectrum of iron, for instance.

Prof. J. Larmor called attention to the fact that radio-activity was not the only cause leading to discussion in these matters, It merely constituted a new group of facts fitting into an old theory. Faraday was really the founder of the electron theory, and he enunciated it when he stated that the separation of matter was proportional to the separation of electricity. Clerk Maxwell, too, wanted to postulate electrons, but they would not fit into his scheme. He (Prof. Larmor) then referred to the beautiful bell analogy of the atom, and said that everything depended on whether the bell was hung on to something else, or whether it was really the atom itself.

Lord Kelvin could not believe that the mere motion of electrons gave the widely different properties and degrees of stability which we knew belonged to different kinds of matter. Nor could he believe that radio-activity was a mere residue of the kinetic energy of the atom, for if so, how could an electron be thrown off with the velocity of light? He preferred rather to regard the atom as a big gun loaded with a shell which again contained a charge, for when the electron was thrown off it did not cause the bursting asunder of the atom any more than the firing of the gun effected its destruction. The electron itself, however, did change its original nature, in exactly the same way as the shell broke into pieces when it exploded.

* For the Report of this Discussion and of the two Papers which follow, read before the British Association (Section A), Leicester Meeting, we are indebted to the courtesy of the Editor of the *Electrician*.

His gun had probably been loaded before there were sun, stars, or any of the things that we now know, and it only required contact with matter to release the trigger and fire off the shell.

Prof. RUTHERFORD replied very briefly.

ON THE VARIABILITY IN THE PRODUCTS RESULTING FROM CHANGES IN RADIUM EMANATION.

By Sir WILLIAM RAMSAY, F.R.S.

THE author commenced by reminding his audience that radium, actinium, and thorium all yield helium, and then proceeded to describe the results of experiments which are nothing short of remarkable. It is known, of course, that the emanation decomposes water with the liberation of excess of hydrogen, but where this excess of hydrogen comes from nobody knows. Sir William Ramsay exposed a solution of copper sulphate to the emanation for about a month, and at the end of that time the residue obtained gave the spectra of both sodium and lithium. The experiments were repeated three times, and the results were perfectly consistent in each case. The presence of sodium was not, of course, surprising, as the containing vessels used were composed of glass, but all the materials were tested for lithium, and there was not a trace before the experiments were commenced. Nevertheless, Sir William Ramsay expressed a doubt as to whether the quantity of sodium found could have all come from the glass, and he is going to undertake further investigations in this direction. His next experiment was with copper nitrate, when lithium was again detected after a solution had been exposed to the emanation. Fresh copper nitrate not so treated with the emanation showed no sign of the presence of lithium. In both cases, however, sodium sulphate was detected, but the treated substance showed just twice as much (1·6 mgrms.) as the untreated substance. On evaporating water treated with the emanation 0·3 mgrm. of solid was obtained, while the inactive gas produced was neon with a trace of helium. Gases from the treated copper nitrate solution contained argon, with possibly a trace of neon. He remarked that 1 cc. of emanation gives off three and a-half million times as much energy as 1 cc. of a mixture of hydrogen and oxygen when exploded, and suggested that some of this vast amount of energy might account for the presence of the elements which he had found.

The Hon. R. J. STRUTT confessed that he could not find any source of error in Sir William Ramsay's experiments to account for the presence of neon in the case of water and emanation. He made a rough calculation in order to determine how much air would be required to provide the amount of neon (0·5 cubic mm.) obtained by Sir William Ramsay, and found that it was about 100 cc. In these circumstances, he was sure that there could not have been such a large leakage of air to the apparatus as would account for this quantity. He further mentioned that there was quite sufficient lithium in quartz vessels to give a very distinct spectrum.

Prof. RUTHERFORD complained that the amount of radium in the possession of experimenters was deplorably small. There were only about two laboratories in the world that were in a position to repeat Ramsay's experiments, and if only an experimenter could have a grm. instead of 100 mgrms. at his disposal there would be a very great deal more work done.

Prof. H. E. ARMSTRONG, F.R.S., put forward the suggestion that the so-called inert gases are in reality very active, and that they are not monatomic at all.

In reply, Sir WILLIAM RAMSAY said that helium, when passed through a bath of liquid hydrogen, gave up a considerable amount of krypton.

THE DENSITY OF ETHER.

By Sir OLIVER LODGE.

THE author pointed out that the theory that an electric charge must possess the equivalent of inertia was clearly established by J. J. Thomson in the *Phil. Mag.* for April, 1881, and that the discovery of masses smaller than atoms was made experimentally by J. J. Thomson, and communicated to Section A at Dover in 1889. The theory that the corpuscles so discovered consisted wholly of electric charges was sustained by many people, and was clinched by the experiments of Kaufmann in 1902. The concentration of the ionic charge, required to give the observed corpuscular inertia could be easily calculated; and, consequently, the size of the electric nucleus, or electron, was known. The old conception that a magnetic field was kinetic had been developed by Kelvin, Heaviside, FitzGerald, Hicks, and Larmor, most of whom had treated it as a flow along magnetic lines; though it might also, perhaps equally well, be regarded as a flow perpendicular to them and along the Poynting vector. The former doctrine was sustained by Larmor, as in accordance with the principle of Least Action, and with the absolutely stationary character of the ether as a whole; the latter view appeared to be more consistent with the theories of J. J. Thomson. A change in motion was well known to be surrounded by a magnetic field; and the energy of the motion could be expressed in terms of the energy of this concomitant field, which again must be accounted as the kinetic energy of etherous flow. Putting these things together, and considering the ether as essentially incompressible—on the strength of the Cavendish electric experiment, the facts of gravitation and the general idea of a connecting continuous medium—the author reckoned that to deal with the ether dynamically it must be treated as having a density of the order of 10^{12} grms. per cc. The existence of transverse waves in the interior of a fluid could only be explained on gyrostatic principles, *i.e.*, by the kinetic or rotational elasticity of Lord Kelvin. And the internal circulatory speed of the intrinsic motion of such a fluid must be comparable with the velocity with which such waves were transmitted. Putting these things together, it followed that the intrinsic or constitutional vortex energy of the ether must be of the order 10^{33} ergs per cc. Thus, every cubic mm. of the universal ether of space must possess the equivalent of a thousand tons, and every part of it must be squirming internally with the velocity of light.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

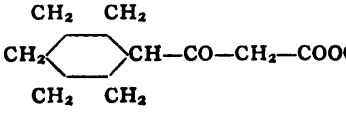
NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlv., No. 3, July 16, 1907.

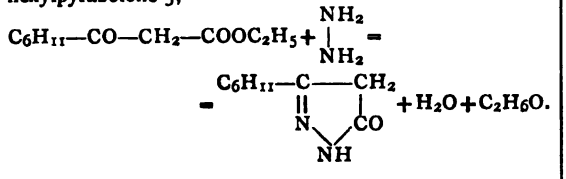
Analysis of Selenium Hexafluoride.—Paul Lebeau.—The gaseous mixture obtained by the action of fluorine upon selenium contains varying quantities of silicon fluoride, which may be eliminated by means of water. The gas can then be liquefied with liquid oxygen and the vapour received into empty flasks. When thus fractionated the gas shows very appreciable differences in density between the first and last fractions. If the gas is heated in a Jena glass vessel a mixture of gases having a volume about one and a-half times that of the original gas is obtained, consisting of silicon fluoride and oxygen. The results of different experiments are not absolutely concordant, and they do not lead to the formula SeF_6. When the gas is heated in tubes of pure silica the quantities of oxygen and silicon fluoride formed are approximately those indicated by the equation

$2SeF_6 + 3SiO_2 = 3SiF_4 + 2SeO_2 + O_2$, but the values found
4 vol. 6 vol. 2 vol.
for oxygen are a little high and for fluorine a little low. To determine the fluorine and silicon in one sample of gas it was decomposed by sodammonium in liquid ammonia. The solution then contained selenide and fluoride of sodium, and a small quantity of selenium is converted into selenite. The selenium of the selenide was precipitated by a current of air, and that of the selenite was determined in the form of sulphide, while the fluorine was separated and weighed as calcium fluoride. The results thus obtained all showed that the gas contains some oxyfluoride, which would be difficult to separate if the boiling-points are not far apart (*cf.* the boiling-points of sulphur hexafluoride and oxyfluoride). The gas in presence of mercury and glass undergoes a purification, and its density rises, which explains the very satisfactory results which Prideaux obtained when he determined its physical constants.

Ethyl Hexahydrobenzoylacetate.—A. Wahl and A. Meyer.—The condensation of dry ethyl hexahydrobenzoate and acetate by means of sodium on a water-bath yields a small quantity of a substance with boiling-point 140—143° under 25 mm. pressure. On analysis this gives the values corresponding to ethyl hexahydrobenzoylacetate :—

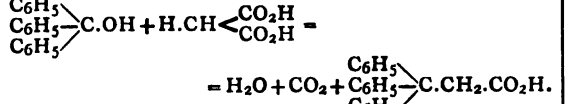


The yield is very poor. Methyl hexahydrobenzoylacetate may be prepared similarly. These two substances when diluted have an odour recalling that of leather. They are β-ketonic esters; they react with hydrazine hydrate, giving a crystalline compound corresponding to 3-cyclohexylpyrazolone-5,—

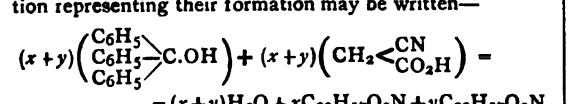


They also give crystalline copper salts with an aqueous solution of copper acetate.

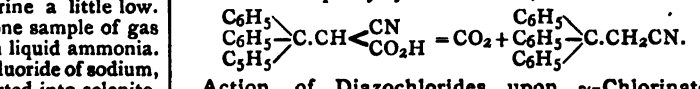
Triphenylcarbinol. Action of Malonic and Cyanacetic Acids.—R. Fosse.—Malonic acid transforms triphenylcarbinol into Henderson's triphenyl-β-propionic acid,—



When the two reagents are heated together an intense red coloration is produced; it fades after a time, and a slightly coloured product remains which is completely soluble in alkalis. Thus, apparently, an unstable intermediate product is first formed. When cyanacetic acid is substituted for malonic acid two isomeric acids of formula $C_{22}H_{17}O_2N$ are formed, which may be called A and B triphenylmethylcyanacetic acids respectively. The equation representing their formation may be written—



When the group CO_2 is removed from these acids the products are two isomers of formula $C_{12}H_{17}N$, which are isomeric with 1.1.1.3-triphenylpropane nitrile obtained from normal triphenylcyanacetic acid,—



Action of Diazochlorides upon γ-Chlorinated Acetoacetic Esters.—G. Favrel.—γ-Chlorinated acetoacetic esters react with diazochlorides giving the 3-hydrazones of the chloro-1-butane dione 2.3-esters. Under the same conditions the α-chlorinated acetoacetic esters give the hydrazones of chlorinated glyoxylic esters, and thus this reaction provides a means of distinguishing between the α- and γ-chlorinated esters.

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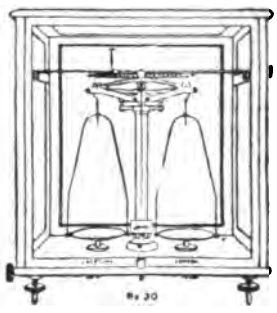

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THE CHEMICAL NEWS.

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NOTE ON THE USE OF THE RADIOMETER IN OBSERVING SMALL GAS PRESSURES. APPLICATION TO THE DETECTION OF THE GASEOUS PRODUCTS PRODUCED BY RADIO-ACTIVE BODIES.*

By Sir JAMES DEWAR, M.A., Sc.D., LL.D., F.R.S.

SOME time ago I exhibited at a Soirée of the Royal Society a few experiments with the Crookes radiometer, the object being to show that when helium is the residuary gas filling the instrument, an attached charcoal condenser, even when placed in liquid hydrogen, is unable to diminish the pressure by absorption to such an extent that the radiometer will not rotate (when subjected to the concentrated beam of an electric arc lamp focussed upon the black surface of the mica vanes)); while, on the other hand, if the gas instead of being helium is hydrogen, all radiometer motion is suspended. Even when the charcoal condenser of the helium radiometer was cooled in solid hydrogen under exhaustion so that a temperature of 15° absolute was reached, the rotation of the instrument was still very marked. If the radiometer is repeatedly washed out with the mixed oxygen and nitrogen got from the evaporation of liquid air, the charcoal and the whole of the glass being thoroughly heated and the apparatus finally exhausted to a fraction of a millimetre, and sealed off, then, on placing the charcoal tube in liquid air, generally after an hour or two, the vacuum is so high that no motion is induced by the beam of the electric arc. But if instead of liquid air the cooling agent is liquid hydrogen, then two minutes' immersion is sufficient to effect the same result, provided the radiometer is small and the gases get down a quill tube direct into the charcoal. Instead of the gases from liquid air being used to clean out the radiometer as described, it is for some purposes better to seal on a side tube containing perchlorate of potassium, which, when heated, gives pure oxygen. Further, in many experiments, it is advantageous to exhaust the radiometer with its little charcoal condenser by means of a larger quantity of charcoal placed in liquid air for a night, and then to seal the latter off before cooling the special charcoal bulb attached to the radiometer. When a McLeod gauge was sealed on to the end of the bulb containing the charcoal condenser which is cooled in liquid air (no stopcocks of any kind being used), all the mercury vapour was eliminated from the radiometer, and the pressure of the permanent gas was found to be 0·00001 mm., or one seventy-six millionth of an atmosphere. In this condition the radiometer moved when the image of the poles was focussed on the black vanes, and after some fifteen minutes' heating the pressure was found to be only one twenty-five millionth of an atmosphere, and the pressure remained at this after ten hours' cooling of the charcoal condenser in liquid air. The gas produced was no doubt hydrogen, got from the lamp-black of the mica vanes, this being the first time the instrument was used. As a rule, the radiometers require to be re-filled, exhausted, and tested more than once in order to get the motion reduced to a minimum. The importance of the removal of traces of gases like helium, hydrogen, or neon is shown from the fact that a radiometer which has the charcoal removed from the attached bulb, and the latter cooled in liquid hydrogen (the instrument having been previously filled with dry air and exhausted to a fraction of a millimetre of mercury), will not reach such a vacuum as to stop the radiometer motion. Now, as the pressure of nitrogen at the boiling-point of hydrogen must be of the order of a millionth of a millionth of an atmosphere, the action must come either from uncondensable gases, or the persistent adhesion of gas molecules to the glass and vanes of the radiometer, or to some solid matter volatile under the conditions of the experiment. The lowest pressure reached in a charcoal vacuum after ten minutes' cooling in solid hydrogen was still one hundred millionth of an atmosphere. The pressure observed is thus far too high, and it may be that some of this is due to hydrogen coming from the charcoal. To get really high vacua by the charcoal method, even when liquid hydrogen is the cooling agent, it seems necessary to allow the absorption to go on for an hour or more; when the space to be exhausted is relatively large and where narrow tubes or orifices constitute part of the apparatus, as in the McLeod gauge. Further, the presence of any organic matter on the vanes is fatal. No amount of cooling of the charcoal in liquid hydrogen of a radiometer filled as usual and tested in the ordinary manner, in which the vanes were made of pith, make a vacuum sufficient to stop the radiometer motion. The concentrated beam, each time it was applied, was generating gas. In all the experiments the arc used was expending 10 ampères, and the focus was adjusted to about 3 feet from the lamp. The radiometers had a volume of from 150 to 20 cc.

Finding the McLeod gauge very difficult to use, a new method of defining the maximum limit of the working pressure (under the defined circumstances) depending upon the vapour-pressure of mercury was devised. For this purpose a side tube was sealed on to the top of the radiometer, and this, after being bent twice at right angles, ended in a little bulb containing a globule of mercury. After the radiometer and charcoal were heated and exhausted and repeatedly washed out with the gas from liquid air, the charcoal was cooled in liquid air and the mercury allowed to distil for an hour or two. After this treatment, on cooling the mercury with liquid air, the radiometer in a short time became inactive. In this condition the mercury was placed in an alcohol bath at −80° C., and the temperature allowed to rise slowly.

In this way it was found the radiometer action began in the instrument used at −23° C. The pressure of mercury vapour for the temperature derived from the Hertz formulæ is found to be about a fifty millionth of an atmosphere. All the time of the experiment the mercury vapour was being sucked out of the radiometer by the liquid air cooling of the charcoal tube so that the pressure might be less than the saturated pressure. This result at once suggested that the method ought to be applicable to the detection of the gaseous products derived from the transformation of radio-active bodies. In order to test this application, a side tube containing a little radium bromide was sealed on to the bottom of the charcoal condenser, in order to remove the emanation by absorption in the charcoal kept in liquid air. The radiometer, after thorough washing with the gas from liquid air, heating, and exhaustion by a subsidiary charcoal condenser placed in liquid air that was sealed off, was found inactive after the small charcoal receptacle was cooled for an hour in liquid air. The radiometer was again tested after standing fifteen hours, and was found to be quite active. It would seem that the gas produced must be hydrogen, helium, or the alpha particles. In order to eliminate any hydrogen that might be produced, the charcoal condenser of the radiometer was transferred from liquid air, in which it had been kept for some two days, into liquid hydrogen. After half-an-hour's cooling the motion was active when the image of the arc lamp was focussed on the black surface of the mica vanes of the radiometer, and even after one hour's immersion of the charcoal in the liquid hydrogen the motion suffered no diminution. The active gas must therefore have been helium, along with it may be the alpha particles; unless one is being deceived by some solid deposited on the radiometer vanes sufficiently volatile when the arc light is concentrated on them to cause the motion. A similar radio-

* A Paper Read before the Royal Society, June 27, 1907.

meter to that which was used in the radium experiment had a side tube attached containing some 50 grms. of thoria, and after the usual treatment was found inactive. After keeping a fortnight it is now active, but I have not had the opportunity of cooling the charcoal in liquid hydrogen, so that the possibility of the gas being hydrogen has not been eliminated. We might anticipitate that monadic gases of the type of helium and mercury would be more effective than the ordinary gases in inducing radiometer motion. A radiometer with a helium residue will still work under fixed conditions when the gas pressure is four or five times higher than one containing an oxygen residuum. Again, the sensibility of the instrument ought to increase, provided it was subjected to the same intensity of radiation while immersed in liquid air or liquid hydrogen.

The experiments, in any case, seem to show that the radiometer may be used as an efficient instrument of research for the detection of small gas pressures and the study of radio-active products. For quantitative measurements the torsion balance or bifilar suspension must be employed. It would be interesting to repeat light repulsion experiments in the highest attainable charcoal vacuum. Later on I hope to extend the investigation.

THE NATURE OF IONISATION—IONOMANIA.*

By HENRY E. ARMSTRONG.

In his imaginative work on the hypothetical entities termed electrons, in the opening sentence of the chapter which bears the heading "Ionisation of Gases," Sir O. Lodge tells us that "It is constantly necessary to speak of the air being 'ionised' by the passage of rays and many other processes. The term means the molecules are split up or dissociated into their constituent atoms."

The term certainly is used by many in this sense at the present day; yet inadvertently, I venture to contend.

The word "ion" was introduced in 1834 by Faraday in the immortal seventh series of his researches; it was never verbalised by him—I believe advisedly. He was content with "electrolyze." Why should not we be? Faraday coined the words "anion" and "cation," because he felt, he says, that the terms "electro-negative" and "electro-positive" were much too significant for the use to which he would have to put them. His explanation is worthy of notice in these days of uncontrolled speculation and loose reasoning, "for though the meanings are perhaps right, they are only hypothetical, and may be wrong; and then, through a very imperceptible but still very dangerous because continual influence, they do great injury to science by contracting and limiting the habitual views of those engaged in pursuing it." We moderns have no such scruples; our guiding principle seems to be that language is given to us to disguise our thoughts. Every vague conception as it arises must at once be embodied in an ambiguous new word, so that a reader of present-day "scientific" literature often finds himself in a maze of "jargonese." It will be necessary soon to request the Royal Society to maintain a dictionary of terminological inexactitudes as a key to its *Proceedings* and to the publications of scientific bodies.

Surely we have no need to imply more by the term "ionisation" than that the medium is in a state in which it will conduct electricity? We know no more! When a man and his wife have bought Cook's tickets and packed their luggage, they are ionised-ready to travel; but nothing shows them to be divorced. If we have need to introduce the conception of atomic divorce, let us frankly say so and straightforwardly use the word "dissociation." We cannot do better than follow an example set us by Faraday, and, as far as possible, seek to use only such terms as are at the same time "simple in their nature, clear in their reference and from hypothesis." (Footnote, §666, Series 7).

* A Paper read before the British Association (Section B), Leicester Meeting, 1907.

I cannot discover, although I have read the Papers many times during the past twenty years for the purpose, that Faraday ever conceived of the ion as a restless wanderer, as a solitary fragment; on the contrary, he appears to have thought of the ion as always accompanied or conducted, and as only delivered up at the boundaries—as separated during electrolysis, *e.g.*:—

> § 665. The chloride of lead is an electrolyte, and when electrolyzed evolves the two ions, chlorine and lead.
>
> § 827. If one ion be combined in right proporptions with another strongly opposed to it in its ordinary chemical relations, *i.e.*, if an anion be combined with a cation, then both will travel, the one to the anode, the other to the cathode of the decomposing body.
>
> § 828. If, therefore, an ion pass towards one of the electrodes, another ion must also be passing simultaneously to the other electrode, although, from secondary action, it may not make its appearance.

He distinctly recognised that "attraction of aggregation" lay at the root of electrolytic phenomena—thus he remarks:—

> It is a remarkable circumstance that in gases and vapours, where the attraction of aggregation ceases, there likewise the decomposing powers of electricity apparently cease, and there also the chemical action of quantity is no longer evident. It seems not unlikely that the inability to suffer decomposition in these cases may be dependent upon the absence of that mutual attractive relation of the particles which is the cause of aggregation.

Faraday, in fact, was a pronounced associationist, not a dissociationist. It cannot well be argued that the conception of dissociation was not in his mind; had he foreseen the need of any such explanation he would probably have had little difficulty in formulating it. In his time, chemistry and physics were united sciences and were ionised for joint service, able and willing to co-operate; now they are all but dissociated, and chemistry is cold-shouldered by physics. The consequences of the lack of appreciation and understanding are most unfortunate; I believe really serious. Physicists soar in a mathematical empyrean and have no regard for the plain facts of chemistry. Although they have their being by it and live by it, organic chemistry is tabooed by them. The tangible test-tube has no charms in face of the galvanometer and electrometer; indulgence in speculative lucubrations on the wanderings of a spot of light is too fascinating an occupation.

During the past twenty years I have steadily maintained that the doctrine of electrolytic dissociation is destitute of common-sense. I have discussed the subject on several occasions, and pointed out the inconsistencies, particularly in my Address to the Chemical Society in 1895. I come here to-day, advisedly, to challenge those who accept the creed to reconsider the evidence on which their faith is based. It will not surprise me to be told that faith is something that cannot be based on evidence—merely a longing or desire to believe, felt with special acuteness when facts are inconsiderately in opposition to fancy.

So far as I am aware, the arguments on which the hypothesis is really based are:—(1) The existence of Ohm's law, and (2) the assumption that any electromotive force, however small, will condition sensible electrolysis. Fitzgerald disposed of the first in 1890 (*B.A. Reports*, p. 143; compare my Address, p. 1131) by showing that a modified Grothus hypothesis would fit the facts. As to the second, as it is impossible to avoid some polarisation, the fact cannot be regarded as established. The Helmholtz experiment on which reliance is placed cannot be regarded as irreproachable, it being impossible theoretically to remove a gas entirely from solution by any solvent in contact with the liquid.

Mr. Whetham's thermodynamic missiles have no terrors for me; they are mere bombastic shells. To tell us that,

whatever the process, such and such must be the case, is futile; what we are concerned with is the process. Unless I am altogether mistaken, thermodynamics can tell us nothing of this. Thermodynamic arguments at their best afford but scant comfort to those in search of explanations.

It is the great merit of Arrhenius to have recognised that electrolytic conductivity and chemical activity *se confonde*, as he puts it; that is to say, they are phenomena of the same order. All the conclusions arrived at carry us no further. The dissociation hypothesis was only a way of stating this generalisation; had Arrhenius been a chemist he would never have formulated it, as he would have realised that the hypothesis did not satisfy the postulates generally. At best it was an ingenious paraphase of conventional language in stilted phraseology calculated to mislead the unwary.

Gradually, facts have been accumulated which, I believe, constitute a practically complete refutation of the hypothesis and serve to show that chemical interactions—as Faraday f-resaw—are dependent on "mutual attractive relations of the particles," not on dissociation in the sense contended by the Arrhenius-Lodge school. This school assumes that the hydrolytic activity of acids is that of the dissociated hydrogen ions. Hydrolysis can be effected, however, by other agents—in the case of sugars, for example, by enzymes; but the dissociated hydrogen ions should be alike from whatever source they are derived, and it is in accordance with this conclusion that acids may be used without distinction, differing only in the degree of activity which they manifest. Enzymes, however, act selectively; therefore their action cannot be ascribed to dissociated hydrogen ions. Moreover, there is evidence to show that enzymes become associated with the compounds which undergo hydrolysis under their influence; they are not only strictly selective in their action, but are also and only controlled by substances which are of the same configuration as the compounds upon which they act. As there is much evidence that acids can combine with various hydrolytes, there is every reason to suppose that hydrolysis by acids also involves the association of the hydrolyte with the acid.

According to the dissociation hypothesis, the hydrolytic action of an acid should be repressed by salts containing the same anion—the contrary is commonly the case. The increased activity can be accounted for simply and satisfactorily on the assumption that the salt is hydrated in solution, and that by withdrawing water it raises the concentration of the acid.

Much evidence has been accumulated of late showing that no special distinction is to be drawn between dilute and concentrated solutions and that properties vary continuously throughout all degrees of concentration. The difficulties met with in the past in dealing with concentrated solutions have arisen not only from the existence in them of polymerised molecules, but also from the circumstance that the formation of hydrates has been left out of account; and because solutions have been considered with reference to their volume instead of with reference to the mass of the solvent. The change in the solvent has not been sufficiently considered, and the mistake has been made of assuming that liquids are comparable with gases; a preposterous contention.

It was suggested by Fitzgerald that if the molecules in an electrolyte drew one another apart at a rate proportional to the polarisation, the relation between the electric force and the decomposition would be a linear one, so that Ohm's law would be satisfied. In a forthcoming Paper in the *Proceeding of the Royal Society* on the "Discrimination of Hydrates in Solution," Mr. Caldwell and I have argued that the "ionised" molecules are complex, reversible systems formed of solvent and solute under the influence of the force of residual affinity—*e.g.*,—

$$KCl + OH \rightleftarrows KCl{:}OH_2 \rightleftarrows K\overset{H}{\underset{OH}{Cl}} .$$

As such systems break down under the influence of the current, new ones to take their place must arise spontaneously in the solution; the molecules therefore would draw one another apart at a rate proportional to the polarisation.

Another point made by Fitzgerald is that:—

> If dissociated atoms are going about in a liquid as in a gas it seems impossible but that they must diffuse at different rates; and that this is not observed seems conclusive evidence against the hypothesis, no matter what else the hypothesis may explain. Consider solution simply. Why does chloride of sodium dissolve in water? There must be some strong affinity between the two of a chemical or semi-chemical nature to break up the cohesion of the crystal; and it seems reasonable to assume that this same affinity keeps the molecules of sodium chloride moving about among the water molecules, so that they diffuse about. Now, if the forces drawing them about be independent of the nature of the molecule, most of the phenomena explained by gaseous laws are explained. Pressure of a gas depends, at any temperature, on the number of molecules and not on their kind. This is Avogadro's law, by which molecular weights are calculated; and if the forces drawing a molecule about in a liquid are independent of the kind of molecule, the very same law of pressure would hold, the pressure forwards of molecules of different kinds would depend on their number only, and, in the same way as Avogadro's law, would enable molecular weights to be calculated.

The forces drawing a molecule about in a liquid are probably of two kinds, if, as I have contended elsewhere, the molecular composition of the solvent be modified in presence of the solute ("The Origin of Osmotic Effects," *Proc. Roy. Soc.*, 1906, A, lxxviii., 264). In a concentrated region the number of solvent monads would be at a maximum, and these would condition a flow of monads from less concentrated regions, which would tend to force out molecules of solute into these latter. In addition, molecules of the solute would be attracted outward by the force which caused it to dissolve—viz., that existent between it and the solvent. To a considerable extent, therefore, the forces drawing a molecule about would be independent of the kind of molecule.

I do not claim Fitzgerald merely as an advocate of views similar to my own. In this section I shall be understood when I say it is because he always seemed to me to be the least biassed and most capable among us of judging in such matters—perhaps the broadest, most generous and sympathetic mind of our generation.

In the July number of the *Philosophical Magazine* it is contended by Sutherland that electrolytes are completely ionised in solution—completely dissociated into ions, that is to say. The grounds on which he arrives at this conclusion are such that if he extend his examination of the problem he will probably find that, although not dissociated into ions, the molecules are all ionised in the sense that they are all prepared to travel in turn—being somewhat in the condition of a crowd of excursionists waiting at a rail way station ready to enter upon their journey as soon as the trains will take them on.

Far too little attention has been paid as yet to such observations as those made by Brereton Baker on the influence of moisture (coupled with acid or alkaline impurity) in conditioning chemical interchanges, and their bearing on the problem of electrical conductivity in gases. The ocular demonstration given recently by Sir James Dewar of the presence of gaseous matter capable of determining the rotation of the radiometer at exhaustions considerably below those at which the conduction of electricity ceases should once more direct attention to the possible need of referring electrical conduction in gases to the presence of complex tripartite systems of charged molecules (see Note) rather than to that of atomised ions. Exact work in this direction would be most valuable at the present time;

speculative discussion of uncertain results cannot determine the nature of the process of "ionisation," so called.

(NOTE.—It is not customary, I believe, to drag in dissociated ions to explain the action of a condenser; we are satisfied to think of the collection of a charge as dependent on the displacement and distortion—the polarisation—of the molecules in a viscous electrolyte of low conductivity).

CALCIUM: ITS PROPERTIES AND POSSIBILITIES.*

By ARTHUR E. PRATT, B.Sc., A.R.S.M.

General Properties.—Calcium is a silvery white metal readily oxidised in moist air. It is very light (sp. gr. 1·52), fairly malleable, has a high specific heat, and is a good conductor of electricity. It is about as hard as aluminium, but at 400° C. becomes as soft as lead. It is volatile, and can be sublimed *in vacuo* between 700° C. and 800° C., and melts at the latter temperature. It is a very powerful reducing agent.

Calcium Alloys.—The chief effects of alloying calcium with other metals are to produce brittleness, crystallisation, and hardness; to promote oxidation and disintegration on exposure to air; to confer the power of decomposing water and in other ways increasing the chemical activity.

The author's experiments confirm Roberts-Austen's observation that the presence of small amounts of metals of high atomic volume will cause deterioration of the physical properties of metals of low atomic volume. The atomic volume of calcium is high (25·4), and the effect of small amounts on other metals is decidedly prejudicial, provided that the metals in question are pure. The experiments were conducted in a converse manner to Roberts-Austen's, *i.e.*, the constant was a metal of high atomic volume (calcium) instead of being low (gold). In the course of the work the following observations were made. When an alloy is made of calcium and some metal which possesses a chemical property in common with it, an increased activity in the manifestation of that property is noticed in the alloy. This increase appears to be greater than would be obtained by the simple admixture of a more active metal, the presence of calcium usually increasing the activity of the other metal. In some cases the alloy is more active than either of its constituents.

Further, the chemical properties of calcium appear to be more pronounced in an alloy with a metal having an atomic volume closely approaching that of calcium than they are in an alloy of the same percentage with a metal having a much lower atomic value. The two metals in question should be about equally active when unalloyed in the particular property with respect to which they are to be compared.

It is probable that both these principles are general, and not confined to calcium, although more extended research on these lines would be desirable.

Industrial Possibilities.—The most promising applications of calcium are as a reducing agent and for the refining of metals. In the latter case it acts in three distinct ways:—(1) By reducing oxides and sulphides; (2) by eliminating dissolved gases; (3) by forming compounds with certain impurities, thus rendering them less deleterious. All three modes of action are strikingly shown in the case of copper. A suitable addition of calcium will remedy "dry" or "sulphury" copper, give a sound casting, and give a soft and tough ingot with prohibitive proportions of bismuth or antimony, besides restoring ordinary overpoled copper to tough pitch. If excess of calcium is present, however, it induces brittleness on its own account.

With one or two doubtful exceptions, no alloy of calcium has shown any promise of commercial utility so far as physical properties are concerned, its only likely application in this direction being its hardening property.

* A Paper read before the British Association (Section B), Leicester Meeting, 1907.

ON SUBSTANCES WHICH FORM THREE DIFFERENT LIQUID PHASES.*

By Dr. F. M. JAEGER.

THE results now recorded arose originally during an experimental investigation into certain theoretical objections which occurred to the author in connection with Bömer's method for detecting the adulteration of animal fats with vegetable fats. During this work the series of fatty esters of cholesterol and of Windaus's two phytosterols of Calabar fat were prepared, and the observation of the brilliant colour changes which occur on melting the cholesterol esters led to the study of the liquid phases of these substances. The colour changes in question occur with greatest brilliance with cholesteryl cinnamate, and were demonstrated to the audience.

The colour changes are due to the fact that the substances which exhibit them yield on melting several strongly doubly refracting liquid phases; the liquid phase stable at higher temperatures is always singly refracting. Lehmann showed by the micro-crystallographic examination of the caproic ester that two doubly refracting liquid phases exist, and that of these one is in meta stable equilibrium with the solid substance.

The author has, however, found that in the cases of a number of the esters in question three liquid phases occur, and are in perfectly stable equilibrium with the solid phase; of the three liquid phases two are doubly refracting, and consist of aggregations of liquid crystals, whilst the third is always singly refracting, but often much more viscid than the doubly refracting phases. The colour changes occur at the transition temperatures—or, rather, at a few degrees below those temperatures—whilst the two liquid layers are separating from each other.

The transitions of phase are in many respects analogous to those occurring with polymorphous substances, so that stable and metastable equilibria and therefore also cases of monotropy and enantiotropy occur. It is, however, remarkable that a new kind of equilibrium is observed with these substances; this the author terms "prostable equilibrium." A prostable phase resembles a metastable phase in that both can be experimentally realised only as the result of a temperature change in one direction; the two kinds of phase differ in that the prostable phase can only be obtained as a result of raising the temperature. The formation of a prostable phase therefore occurs before and after that of the stable phases during a rise of temperature. This was demonstrated to the audience with the aid of cholesteryl laurinate and illustrated by means of the vapour-tension curve of the ester.

With some of these esters the author has further observed that the solid phase can be heated to above the melting-point without melting; cholesteryl laurinate can thus be heated to 5° above the highest transition temperature without the solid phase entirely disappearing. Similar retardation phenomena occur in other cases, and their occurrence can be conveniently illustrated by means of the vapour-tension curves of the α-phytosterol esters.

* A Paper read before the British Association (Section B), Leicester Meeting, 1907.

Alloys of Nickel and Tin.—Em. Vigouroux.—When mixtures of nickel and tin, containing between 40 and 50 per cent of the latter, are heated in a current of pure hydrogen, from the resulting product a compound of the composition Ni_3Sn_2 may be isolated by the action of hydrochloric acid. The alloy is very easily crushed in a mortar and fragments of it may be broken off with the fingers.—*Comptes Rendus*, cxlv., No. 4.

ANALYSIS OF PRODUCER GAS FOR THE POWER ENGINEER.

By H. PROCTER SMITH, F.C.S.

IN the writer's opinion there is nearly always a gap between the results given by a chemist and the data required by an engineer to act upon the information given, and, as a rule, this gap can be filled much more easily by the chemist than by the engineer, and if it *were* filled by the mutual co-operation of the chemist and the engineer there is no doubt that valuable information would be acquired, and would eventually bring the chemist and the engineer to be recognised as main factors in helping to swell the profits of an industrial concern, and not as at present mere "non-producers" and a necessary nuisance.

This is illustrated in a very striking manner since the rapid advances which have been made in utilising producer gas as a motive-power in a gas-engine.

In this instance we have a chemist who makes analyses of samples of the gas and perhaps offers suggestions as to the reason for an increased percentage of carbon dioxide, or of hydrogen, and so forth, and who reports to the engineer the relative quantities of carbon dioxide, carbon monoxide, hydrogen, marsh gas, &c., but, as a rule, this is all.

Now, the engineer knows that he wants a gas with as large an amount of combustible as possible, and also knows that the gases, carbon monoxide, hydrogen, and marsh gas are combustible, but from looking at the mere percentages of these gases he cannot, as a rule, form much idea of the amount of horse-power which this gas will develope in his engine, and the factors given below are such as will enable either the engineer or the chemist to rapidly convert the gas analysis into a heat analysis, and from that to a power analysis.

The power capable of being developed by a gas is a ratio of its heating value, and this value is in relation to the amounts of its constituent gases. An element when combining with oxygen evolves a certain definite amount of heat, and if this change is brought about rapidly also light, when the process is termed "combustion."

With the commoner elements—carbon and hydrogen—use is made of this reaction to generate heat, and the elements are termed *fuels*. Coal is a mineral consisting chiefly of carbon and hydrogen, and may be ignited and burnt in air with the generation of heat. Coal may also be partially burnt in a closed vessel termed a "gas producer," and converted into gas which may be burnt and converted into power apart from the vessel in which the gas is generated.

The amount of heat so generated is expressed in two chief units, viz.:—

British Thermal Unit (B.T.U.), which is the amount of heat required to raise 1 lb. of water 1° F.

Kilogramme Calorie, which is the amount of heat required to raise 1 kilogrm. of water 1° C.

The water in each case being at its point of maximum density, 39·2° F. or 4° C.

The heating or calorific value of carbon is 14,544 B.T.U.; that is to say, if 1 lb. of carbon was burnt in oxygen or air it would generate enough heat to raise 14,544 lbs. of water 1° F.

To consider now the combustible gases:—

	B.T.U. per lb.
Carbon monoxide	4,386
Hydrogen	61,524
Marsh gas	24,021

That is, the heat generated from the above gases in *parts by weight*; but as we generally measure gas these figures require to be converted into the B.T.U. or calories which are developed by burning 1 cubic foot or 1 cubic metre of the gas.

Further, in burning all substances containing hydrogen the combustion produces water, and if, as is generally the case, the final temperature is above 212° F., that water is converted into vapour (steam) and passes off in the waste gases. Now, the conversion of water at 212° F. into steam at 212° F. absorbs a large amount of heat termed "latent heat," which can only be recovered by condensing the steam, and thus the *available* calorific value produced by burning hydrogen is lowered, and therefore in all compounds containing hydrogen we have a *total* and an *available* calorific value.

The following factors serve to convert any of the gases, hydrogen, carbon monoxide, or marsh gas, directly into terms either B.T.U.'s or calories:—

	B.T.U. per cubic foot.		Kilogrm.-calories per cubic metre.	
	Total.	Available.	Total.	Available.
Carbon monoxide	3·419	3·419	30·43	30·43
Hydrogen	3·473	2·924	30·91	26·026
Marsh gas	11·278	10·133	100·38	90·225

To convert | Calories per cubic metre into B.T.U. per cubic foot multiply by 0·11235.
B.T.U. to calories multiply by 0·252.
Calories to B.T.U. multiply by 3·968.

To show how such a calculation may be worked, suppose we have a sample of Mond gas of the following composition:—

	Per cent.		B.T.U. per cubic foot.	
			Total.	Actual.
Carbon dioxide ..	12·9 ×	—	Nil	Nil
Carbon monoxide	13·2 ×	3·419	45·14	45·14
Hydrogen	24·8 ×	3·473 or 2·924	86·13	72·51
Marsh gas	2·3 ×	11·278 or 10·133	25·94	23·30
Nitrogen	46·8 ×	—	Nil	Nil
	100·0		157·21	140·95

Thus, by a few very simple calculations it is possible to convert a chemical analysis into a heat analysis.

Then for power conversion:—

1 B.T.U. = 778 foot-lbs.

1 Horse-power = 33,000 foot-lbs.

Thus, the *theoretical* power analysis is merely a matter of proportion.

It must, however, be borne in mind that the theoretical and practical results, otherwise the efficiency of the best heat engine of this type, seldom exceeds 25 per cent, but to the gas-power engineer the calorific power rather than the chemical analysis of a gas is what is required.

The Fresenius Chemical Laboratory at Wiesbaden.—During the Summer Term, 1907, the Fresenius Chemica Laboratory was attended by twenty-eight students. Of these, eighteen were from Germany, two from England, two from France, two from Holland, one from Hungary, one from Norway, one from Russia, and one from East India. There were three assistants in the Instruction Laboratory and twenty-four in the "Versuchsstationen" (Private Laboratories). To the certified staff of teachers belong the Directors, Geh. Regierungsrat Prof. Dr. H. Fresenius, Prof. Dr. W. Fresenius, Prof. Dr. E. Hintz; also Prof. Dr. Med. G. Frank, Dr. L. Grünhut, Dr. R. Fresenius, and J. Huber (Architect). The Winter Term begins October 15th. During the past term, besides the scientific researches, numerous analyses were undertaken in the different departments of the Laboratory (Versuchsstationen) in the interests of trade, industry, mining, agriculture, hygiene, justice, and government.

CONSERVATION OF HISTORIC BUILDINGS AND FRESCOES.*

By Professor A. H. CHURCH, M.A., D.Sc., F.R.S.

The title of this Discourse as announced is in one way too wide, in another too narrow. For "conservation of historic buildings" should be substituted "conservation of urban stonework," and for "frescoes," "wall-paintings."

We have to consider the nature of the attack and of the defence—the weapons and the armour—the damage and its repair.

First amongst the destructive agents at work, I am bound to place sulphuric acid. I own myself a *thiophobist*. Dr. S. Rideal has given an estimate of the amount of sulphuric acid poured year by year into the atmosphere of London by the coal burnt in the Metropolis. His minimum figure is half a million tons, his maximum twice that amount. But before dealing with this branch of the subject in some detail, let me enumerate the chief of the other hostile agents. These are soot and tarry matters from coal-smoke; water, and an abnormal amount of carbon dioxide. Minor enemies, such as hydrochloric acid, nitric acid, and ammonia salts, with sulphuretted hydrogen and sulphurous acid, may be put on one side for the nonce. These assist in doing damage—damage of a special kind and to particular materials, such as metals and organic pigments—but our attention ought to be focussed on the chief mischief-makers. Before dealing with these, I may observe that it is fortunate that nitric and hydrochloric acids exist in but small proportion in the atmosphere of towns, save in the immediate vicinity of certain factories. I say "fortunate," for at present no efficient chemical means of neutralising their bad effects upon stonework seems available. Of course, one may use mechanical methods of protection, but a stone which has been attacked by nitric or by hydrochloric acid does not allow of the entire conversion of its soluble salts into insoluble, nor, in consequence, of its reconsolidation.

Even now I cannot approach closely the story of our arch-enemy, sulphuric acid, without previously saying a few words about soot and tar, about water and carbon dioxide. The important *rôle* of these last in the natural weathering of stone does not need discussion, but water, as the carrier of sulphuric acid, and as the solvent of the sulphates which it helps to form, must not be passed by in silence. Moreover, the condensation of moisture upon the surface of a fresco within a building is most harmful, and, when it cannot be wholly avoided, indicates the desirability of applying some waterproofing material to the surface of the painting. As to soot and tarry matters just named, one has to remember that even the total abolition of smoke from coal would in no way lessen the amount of sulphuric acid produced in the burning of this fuel. The soot and tar of smoke do indeed adhere to stone and discolour and disfigure it, but, except as carriers of acid, they do not corrode it. Here are some figures from the analysis of a strange crust attached to the under-surface of the cornice above the colonnade and below the dome of St. Paul's Cathedral. This crust has been slowly formed by the conversion of calcium carbonate from the Portland stone above the cornice into gypsum. This change has been effected by the acid rain of the City; then the gypsum has entered into solution, which has hung as drip to the lower face of the cornice, until the water has evaporated, and the residual gypsum, dirty with 1 per cent of soot and somewhat less of tar, has formed a stalactitic mass, occasionally reaching 3 inches in depth. The phosphate of lime present has never been dissolved, but represents one of the constituents of the original stone mechanically carried down and entangled in this dark grey stalactitic gypsum. But a visit to St. Paul's is not needed to see what damage is wrought by sulphuric acid even upon Portland stone. Its decay, being regular and even, often passes unnoticed, but may be watched in all parts of London, in balconies, copings, quoins, &c.

Incrustation from Drip below Cornice, St. Paul's.

Carbon	1·01 per cent.
Ammonium sulphate ..	0·93 „
Tar..	0·60 „
Gypsum..	73·80 „
Calcium phosphate ..	2·22 „
Calcium carbonate ..	none

Allow me to direct your attention to the two chief sources of the sulphuric acid found in the atmosphere of towns, and especially in that of London. There is no doubt that the larger proportion of the sulphur present in coal escapes during burning in the forms of sulphuric and sulphurous acids. Some remains in the ash, and this quantity may be increased by mingling slaked lime with the coal. (Lime-water, which has been suggested for this purpose, is far too weak; indeed, 3000 gallons, or 13 tons 8 cwt., would be required to fix the sulphur of 1 ton of coal!) But there is a minor though by no means negligible source of sulphuric acid in the products of the combustion of coal-gas. Since the restrictions imposed on the gas companies of London have been relaxed—that is, since October 1, 1905—the sulphuric acid from this source has trebled in amount, the average during the twelve months preceding the relaxation having been 11½ grains per 100 cubic feet, but in the subsequent twelve months 33 grains. (I have to thank Dr. F. Clowes, Chief Chemist and Superintending Gas-Examiner to the London County Council, for his kindness in supplying me with the official figures). And during the present year so far there have been 43 grains in the same volume of gas. (The corrosion of copper-boilers heated by gas is now so much more rapid that their lives are shortened in the ratio 7 to 2). If sulphuric acid from coal-gas (like that from paraffin oil) contribute in a comparatively small degree to the pollution of the *general* atmosphere of London, yet it exerts a definitely injurious action when produced in close proximity to an easily affected surface, such as that of a fresco, *within* a building. No wonder that the delicate film of calcium carbonate, the distinctive binding material in a fresco, soon perishes under the onset of oil of vitriol. And here let me anticipate, what I might have relegated to a later part of my discourse, namely, a few words concerning the best-known frescoes in the Palace of Westminster. I do this because the question of sulphur in gas happens to have been brought into close connection with these paintings in consequence of a Parliamentary paper published last year (Cd. 3085). For it has been urged, by one who writes in the interest of the gas companies, that "the hydrochloric and nitric acid vapours resulting from the electric arc-lamps in nightly use in London are even more pernicious than the burning of gas as at present manufactured." But it must be remembered that analyses of London air and London rain prove that the proportion of these acids present is quite insignificant compared with that of sulphuric acid. The same writer states that five frescoes in the King's Robing Room in Westminster Palace have required nothing more than the removal of dirt. This remark is made in order to discount a statement of mine in the Parliamentary Paper just named. This statement runs thus: "The increased and increasing consumption of coal in London, and the greater licence allowed to the gas companies in the matter of freeing their gas from sulphur compounds, must result in a serious augmentation of sulphuric acid in the air of the Metropolis." But very much more than the removal of dirt was needed. The frescoes are no longer frescoes. While retaining the aspect of frescoes, they have been transformed gradually into paintings which have had their original binding material replaced mainly by ceresin and paraffin wax, unalterable compounds competent to resist even sulphuric acid. But not only has the painted surface required fresh protection, but the ground itself has had to

* A Discourse delivered at the Royal Institution, April 12, 1907.

be strengthened by similar treatment, the plaster having been in many places "sulphated" and thus rendered rotten. So the writer in the *Gas World* of August 25, 1906, has *not*, as he says, hunted out "this mare's nest," and has *not* furnished a "typical illustration of the reason why what is called 'science' does not carry conviction when dragged into the concerns of everyday life."

And now I turn to another criticism of the already-quoted passage from the latest Parliamentary Paper on Westminster Frescoes. It will be found in the *Journal of Gas-Lighting* for the 21st of August last. The writer, after stating that he is not then disposed to question the opinion that it is sulphuric acid which is the chief destructive agency at work on the Westminster paintings, argues that the greater licence allowed to the gas companies will result in an improvement of the London atmosphere. The line of argument is this—"The use of gas will be extended by the cheapening which the slight increase in the permitted amount of sulphur in the gas involves," and in consequence less coal will be burnt, and there will, therefore, be less sulphuric acid produced and thrown into the atmosphere. For it is admitted on all sides that the burning of coal is the prime source of the sulphuric acid in the general atmosphere. Of course, if gas were made at or near the collieries, and sent in pipes to the big cities, and displaced coal for heating as well as lighting purposes, we should go far to abolish town smoke, and should greatly lessen the sulphuric acid. Unfortunately for the actual cogency of this argument, we find that the three chief gas companies in the county of London have NOT reduced the price of their gas in the smallest degree since the relaxation of the rule about sulphur, while their gas has, during the twelve months ending September 30, 1906, discharged into the air three times as much sulphuric acid (and during the last three months, four times) as it did under the former restrictions. This is, indeed, a retrograde movement.

One word more on this subject. The wall-paintings in the King's Robing Room at Westminster are, or rather were, true frescoes. Yet the *Westminster Gazette* stated, in one of its issues of August last, that a representative of the paper was told at the National Gallery that these works "were not real frescoes, but oil (paintings) on soft plaster." No person of experience and authority in Trafalgar Square could have made so absurd a statement. The paintings referred to, five in number, were executed in true fresco by William Dyce, R.A., four of them between the years 1851 and 1854, while the fifth and largest was completed in 1864.

Before going further, I would direct attention to the amount of calcium carbonate which the minimum quantity of sulphuric acid yearly produced from coal-burning in London might transform into gypsum: 500,000 tons of this acid might destroy 510,200 tons of $CaCO_3$, evolve 204,080 tons of CO_2, and produce 877,544 tons of gypsum. This change is, moreover, accompanied by an expansion, 100 vols. of calcite producing 120 vols. of gypsum. Happily, part of this sulphuric acid passes away harmlessly, yet the havoc done is everywhere conspicuous, on stone, marble, and mortar.

Thus far I have spoken about our chief agent of destruction, sulphuric acid, describing its sources and connecting it with stonework, on the one hand, and with certain mural paintings on the other. Now I purpose dealing with certain preservative and restorative methods, taking, in the first place, stonework into consideration, then mural paintings. My aim will be to describe two methods of treatment only—methods which are not always available, though of wide application.

In reference to decayed stonework, I would name the opening section, "Baryta *versus* Lime." Some persons interested in the preservation of old buildings, and rightly refusing the ignominy of a coat of common oil-paint or of prosaic cement, recommend treating the decayed and decaying stone with lime-wash (not whitewash). The suggestion is an obvious one, but unfortunately this easy process is unsound in theory and ineffective in practice. Moreover, the application of this meagre and indiscriminate lime-wash destroys all the exquisite qualities of tone, colour, texture, and translucency which old stonework may still possess in its age-worn state. And it cannot fail to distort and even obliterate the last surviving traces of surface-enrichment, of mouldings and carvings (*e.g.*, the decaying diaper-work in the spandrils of the great arches in Westminster Abbey). Lime forms a crust on the decayed stone; lime does nothing towards the consolidation of the disintegrated substance; lime is itself subject to the same chemical changes which have injured the stone; lime sooner or later falls off, bringing with it the decayed layer to which it was applied. Mr. Thackeray Turner, one of the most strenuous apostles of the gospel of lime-wash, cited (*The Times*, November, 1904) the case of lime-washed cottages in Wales and Cornwall as evidence of the preservative value of this treatment. But as we are dealing with urban, not rural conditions, such evidence is beside the mark. Baryta, it is true, is a late-comer compared with lime, but it has been used, though in a half-hearted way, for forty-five years. Had it been known earlier to the advocates of lime, it ought to have ousted that earth ere now. Having the choice of two earths, why not use the better? Please visit the eastern walk of Westminster Cloister, and look at what has just been done to the ribs and vault of the bay nearest to the Abbey; no London dirt can turn that prose into poetry.

Let me describe the theory and practice of the baryta treatment of decayed stone. Baryta-water only is used, the liquid being applied, when all dust has been blown away, in the form of extremely fine spray, on very tender surfaces. Where the stone will bear it a rose syringe or even a brush may be used. Indeed, after a few sprayings and the lapse of a week or two, it is generally feasible to adopt the rougher methods. The rationale of the action of baryta is simple. The liquid, which saturated at 16° C. contains about 3 per cent of BaO, is absorbed by the decayed stone, penetrating to some depth, maybe 2 or 3 inches. The baryta forms an insoluble sulphate with the sulphuric constituent of the gypsum and of the other sulphates present, and at the same time calcium hydrate is set free. This probably in part unites with soluble silica, but most of it gradually becomes carbonated, while the calcium carbonate thus regenerated actually reconstitutes the original binding cement of the stone. This description applies especially to sandstones compacted by calcium carbonate; but limestones illustrate the same changes. Unlike water-glass and most of the other preparations which have been used for hardening decayed stone, baryta forms no crust on the surface—indeed, it produces no sensible effect on the outside until it has penetrated to the deeper parts. So when the Dean of Exeter, in his letter published in *The Times* of October 26 last year, stated that "baryta does not strengthen the stone structurally, it forms a scab of the decayed stone on the face of the sound stone, which, as is the case with all scabs, has a tendency to peel off," he could hardly have selected more inappropriate terms in which to describe the action of baryta. The Dean further stated his belief "that the decay at Westminster was comparatively superficial." Surely very few persons would regard a decayed layer 2 or even 3 inches thick as superficial. And he raises the question whether the baryta-treatment, which his friend the late Mr. Micklethwaite told him seems to be successful "so far as we can judge yet," would answer outside a building as well as inside. Here I may cite the case of Chichester bell-tower. On analysing portions of decayed stone from the several faces of this campanile, I found sufficient sulphate present to warrant the application of baryta-water to a trial area. This was done some two or three years ago with so satisfactory a result that last July Mr. Somers Clarke, the architect, decided upon treating the whole of the octagon and the entire north face of the tower in the same way. He wrote:—"The success of the experiment fully justifies this course." There is no need to multiply references to other successful trials of the

use of baryta in strengthening external decayed stonework and stopping further damage, but in the course of the next few years it may be expected that many favourable reports will be forthcoming. Experiments, large and small, are being and have lately been made, and promise well. I have been told of a single failure, but I learnt that the architect in charge expected that the consolidation of the decayed stone would be immediate, and had not waited for the few weeks needed for carbonation to take place. It is proper to add that where decay has resulted from simple weathering—the action mainly of water and carbon dioxide—or from sea-salt, the treatment with baryta is not applicable. Nor should it be forgotten that baryta water is toxic and easily spoilt by exposure to the air. Then, again, there may be too little gypsum present in the decayed stone for an adequate liberation of caustic lime to occur. Without laying down a rule it may be said that where so much as 2 per cent of this sulphate is present, baryta treatment is indicated.

In the case of the Chapter House, Westminster, to which I would now direct your attention, the proportion of calcium sulphate was far more than enough to fulfil this condition of success. Although the exterior of this building, and most of the upper portions of the interior, date only from the time of the restoration carried out by Sir Gilbert Scott, much of the original work of the middle of the thirteenth century remains. The Chapter House is in the custody of H.M. Office of Works. The successive First Commissioners, as well as the permanent officers of that Board, have sympathetically regarded its preservation So when, in 1900, Mr. Micklethwaite pointed out to Mr. Akers Douglas that serious tokens of disintegration were appearing in the early mouldings of the arcading, in the diaper work above, and in the exquisite sculpture of the soffits of the entrance arch, my advice was asked. A few experiments showed that the disintegration and efflorescence were due to the formation of gypsum, which, in some parts of the decayed material, exceeded 17 per cent. The stone, a sandstone, with a calcareous cement, and known as firestone and Reigate stone, no longer contained any calcium carbonate—indeed, had an acid reaction, and yielded to water 4 per cent of saline matter other than gypsum.

Reigate Firestone.

	From the quarry.	From the Chapter House.
Calcium carbonate	9·2 per cent	None
Gypsum	Trace	17·85 per cent
Chlorine	Trace	0·37 ,,
Ammonia	Trace	0·05 ,,
Reaction ..	Neutral	Acid

You will recollect that the conversion of calcium carbonate into gypsum is not only accompanied by the evolution of much carbon dioxide, but that 100 volumes of the former compound expand into 120 volumes of the latter. The rationale of the baryta treatment, to which the interior stonework of the Chapter House was submitted, has been already described; but it may be added that the operations were commenced in May, 1900, continued in 1901, and completed in 1903. Before treatment, a touch of the finger sufficed to bring away the surface of the carving, afterwards the stone was as sound as that newly quarried, and harder. Incidentally it was found that decayed Purbeck marble was equally amenable to treatment; a column at the right-hand wall of the entry having been successively *barytised*. In no instance has there been a sign of subsequent deterioration. Full particulars are to be found (of the operations in the Chapter House) in the Parlimentary Paper, Cd. 1899/1904. It may be of interest to mention that 220 gallons of baryta water sufficed to treat 560 superficial yards in the Chapter House and its inner entry, eight applications being generally made. The cost of the material was quite trivial, the expense of the treatment being practically confined to the cost of labour and scaffolding. Let me add that the cheapest and best source of the baryta is the fused crystalline hydrate, which contains about 58 per cent of oxide, is less liable to carbonation than the ordinary crystals, and corresponds to the formula $BaH_2O_2,5H_2O$.

With regard to the treatment of the decayed limestone of Canterbury Cathedral, and especially of Bell Harry Tower, a few words only are required. Between November, 1901, and June, 1902, I made a series of analyses of decayed stones from this tower, and recommended the architect in charge to adopt the treatment with baryta, as an experiment on a small surface. This was to have been done in the summer of 1902, but I heard nothing further of the matter until more than two years afterwards, when I learned that, under other advice, the discredited process of the late Jesse Rust, described in his incompleted Patent of June 6, 1861, alternate washes of baryta and fluosilicic acid, but modified by using the fluosilicic acid in smaller proportion than he recommended, was to be tried alongside of the simple baryta solution. I have always deprecated the application of a free acid, such as fluosilicic, to stonework injured by sulphuric acid. For it liberates carbon dioxide from any carbonates present, and at least sometimes produces an unsightly white efflorescence. My own patent process of 1862, according to which alternate applications of baryta-water and of a dialysed solution of silica were to be made, causes no efflorescence and no liberation of CO_2, and has been used with success on large surfaces of new stone. But the silica clogs the pores of the stone, and, if employed at all, should be reserved for the final dressing. My own convictions as to the best course to be pursued at Canterbury, as expressed in my letter to *The Times* of November 19, 1904, remain unaltered in the main, although there are cases in which a hydrofuge substance, such as paraffin or ceresin, may be safely used. But I have never found baryta to fail, where its employment was indicated, on calcareous stone. Nor does disruption ever occur with the repeated but reasonable application of baryta-water saturated at 16° C., although I can easily believe that warm and stronger solutions might be dangerous to use.

Last year five bays of the Cheapside frontage of Mercers' Hall were treated with baryta. The stone was suffering from serious decay, so that some loose portions had to be removed. The treatment with baryta was followed, in the case of the three easternmost sections of the frontage, by another treatment intended to render the re-consolidated stone acid-proof. I had used the second method with apparent success, in protecting mural paintings in Westminster Palace. It consists in applying to the surface a paste or ointment of ceresin, a solid paraffin wax from ozokerite. The sample used had a solidifying point of 156° F.; it was made into a paste by taking 4 parts by weight, and melting them in the presence of 1 part of terpene and 16 parts of toluol. The mixture is spread on the stone, and then, after the lapse of twenty-four hours at least, the residual layer of ceresin is driven by heat into the stone. There results a slight deepening of the colour of the surface and a slight marble-like translucency. These changes of tone and colour may be seen on Mercers' Hall by comparing the untreated, the baryta-treated, and the double-treated parts. Ceresin produces a better result than the more crystalline paraffin of the same solidfying point, though the latter is perhaps less liable to be soiled by smoke. It is essential to the success of the double treatment that the calcium hydrate set free by the baryta should be allowed time to become carbonated before the ceresin-paste is applied. The advantage of associating the two treatments lies in this, that while the baryta repairs the damage done by sulphuric acid and reconstitutes the stone structurally, the ceresin waterproofs the surface and prevents further corrosion. Needless to say, it is wiser to waterproof a sound rather than a crumbling stone. What Sir Gilbert Scott tried to do in Westminster Cloisters, with his very perishable so-called preservative, shellac in spirit, was the latter, and led to unhappy results. Thus, even ceresin or paraffin cannot be always recom-

mended, notably where soluble salts and moisture are present. To coat the outer weak layer of stonework decayed to some depth tends to form an easily detachable crust.

However, ceresin alone has been used with apparent success so far in the case of the local Camaru stone of which the Bank of Australasia at Melbourne is built. After due laboratory experiments I recommended this treatment in February, 1903. Mr. Anketell Henderson, the Melbourne architect, tried aluminium oxalate and other solutions, but found, he says, "that ceresin alone resisted the wet of our torrential rains and the erosion of our sandstorms." He emphasises the use of a ceresin of high melting-point to obviate tackiness, and employs an electric heater in his spraying apparatus. Ordinary oil-paint, frequently renewed, fails to preserve the stone in question. Even a solution of ceresin in petrol proved too weak.

We will now turn to the conservation of mural paintings. Besides ordinary oil-painting four methods are, or were, in common use—tempera or distemper, true fresco, stereochrome or water-glass, and the so-called spirit fresco of the late Mr. Gambier Parry. The last-named process or method need not detain us, for, so far, the paintings executed in this way, if the ground or plaster have been properly prepared and protected, require nothing further than cleaning with bread. And if they should suffer injury or need further protection, the diluted medium can be used for these purposes. Owing to causes explained in memoranda addressed to H.M. Office of Works, the two well-known lunettes by Lord Leighton (Arts of Peace, 1881-6, and Arts of War, 1870 80) in the Victoria and Albert Museum, have required cleaning and repairing in the manner indicated. But the long series in the Ambulatory of the Royal Exchange, having been painted on canvas and affixed afterwards to a sound slate backing, have needed no restoration.

The English mediæval wall-pictures found chiefly in churches, but not unknown in secular buildings, are commonly but wrongly called frescoes. They were painted on dry plastered walls with pigments mixed with size or egg-vehicles. By the mistaken use of varnish, by over-drying when on panel, by mechanical injuries, by vibration, by the chemical action of a corrosive atmosphere, and by the penetration of damp or salts from behind or from below, such paintings have generally suffered serious changes, and are sometimes beyond repair. However, there are several ways of consolidating the painted surface and of securing it in position. Before describihg these, and how to choose, in any given case, the most suitable, I would urge the importance of precautionary measures, namely, the disuse of gas, the shutting off from the back and foundation of the wall of all sources of damp, and the avoidance of all further accession of soluble salts, such as nitre, ammonia compounds, Epsom salts, and common salt.

The very worst preparation that can be applied to a damaged distemper-painting on a damp or saline ground, is a spirit varnish such as mastic or shellac, or an oil varnish such as copal. Where damp and saline matters are present, a dilute solution (under 5 per cent) of pure gelatin in very weak spirit may be used; spraying with this liquid kept hot is often successful where the pigments are powdery. Another useful liquid is a 7 per cent solution of casein in very dilute ammonia, containing 1 per cent of glycerin. This preparation is particularly applicable for the treatment of distemper paintings on wood. But when the works to be treated are on a perfectly dry backing free from injurious saline matters, then, and then only, is it safe to apply what may be called a hydrofuge, or waterproofing material to the surface. This we have in the ceresin-paste already described. Occasionally an extremely small addition of copal varnish to this vehicle may be allowed to secure transparency. Indeed, in my earlier operations of this character I have used Gambier Parry's spirit fresco medium, leaving out the elemi, and replacing the beeswax by paraffin or ceresin. But wherever possible nothing but ceresin-paste or ceresin in solution should be employed. After the cleansing of the surface by an air-blast, by spirits of wine, and by bread-crumb, necessary repaints should be executed with powder-pigments mixed with egg-yolk; then the ceresin should be applied. Pigments to be avoided are yellow ochre, raw sienna, terre verte, and ivory black; zinc white should replace flake white.

With regard to the care of water-glass or stereochrome paintings, my experience, confined chiefly to those in Westminster Palace, has been described in full detail in three Parliamentary Papers, Cd. 7651/1895; Cd. 8054/1896; and Cd. 8893/1898. In these memoranda, the treatment of Maclise's great paintings in the Royal Gallery, and Herbert's picture of Moses and the Tables of the Law in the Peers' Robing Room, is explained. But the quite recent operations on other mural paintings executed in the same method may claim our attention for a few minutes. The sixteen pictures in the Peers' and Commons' Corridors, unlike the other wall-paintings in the building, have been protected for many years past by tightly-fitting glasses; still they have undergone, in part since they were glazed, some changes. The lime-plaster ground had become, in places, quite soft by sulphation, while the pigments were here and there powdery. Moreover, the grey bloom, which so often appears on stereochrome paintings, had overspread many large areas of these interesting and attractive historical works. This grey bloom had produced, in the seven pictures of the series which were dealt with last summer, a peculiarly unpleasant disturbance of the balance of light and shade. In many places, notably in the robes of the figures, the deep-shaded portions of the folds had become lighter in tone than the general surfaces intended to be fully illuminated. I have said that in the seven pictures dealt with in 1906 some of the colours were powdery, the pigments chiefly affected being yellow ochre, raw sienna, artificial ultramarine, and ivory black. This class of decay was seen at its worst in the picture in the Commons' Corridor by E. M. Ward, "The Landing of Charles II. at Dover, 1660." A list of the seven paintings cleaned and repaired in 1906 may prove useful for reference. And I would beg those of my audience interested in the subject to inspect the series, and to compare the untreated with the treated examples, premising that the condition of those dealt with was far more unsatisfactory than that of the rest:—

In the Peers' Corridor, four works by C. W. Cope, painted 1859 to 1866: "The Parting of Lord and Lady Russell"; "The Burial of Charles I."; "Charles I. erecting his Standard at Nottingham"; "Speaker Lenthall asserting the privilege of the Commons."

In the Commons' Corridor, three works by E. M. Ward: "The Last Sleep of Argyll"; "Charles II. and Jane Lane"; "The Landing of Charles II. at Dover, 1660."

The same methods of cleaning and reparation were adopted as in other cases. The grey bloom of silica and sulphate of lime was removed by oblique flicking with soft pads stuffed with carded cotton; cleaning with bread, distilled water, and spirits of wine removed dirt and saline matter. The weak places in the ground were consolidated by means of ceresin, while the whole surface finally received a slight protective film of spirit-fresco medium.

In the early part of this discourse I described, out of their proper place, the repairs executed in the five true frescoes by W. Dyce in the King's Robing Room. I now direct attention to another fresco. It was executed in 1872-3 in the church of St. Stephen, Sydenham Hill, by Sir Edward J. Poynter, P.R.A. It occupies a recess on the south side of the chancel. The artist had repaired it in tempera not long after its completion, but it subsequently showed signs of more serious deterioration. I found that the usual causes of injury had been at work. Much gas is burnt in the church, some burners being very near the picture. Soot, tar, cobwebs, and dust were first removed from the painted surface; then the weak places in the ground were strengthened by ceresin, and repairs

done in tempera colours. Finally, ceresin was applied to protect the restored picture.

There are many other cognate topics on which I should have wished to dwell, and other experiments which I should have been glad to show; but time fails me, and these experiments cannot be completed off-hand. But I may be allowed to state that my warrant for standing here to offer observations on certain methods for preserving stonework and paintings is derived from long devotion to these subjects. Half a century ago I read a paper on the induration of stone before the Oxford Architectural Society, while in January, 1862, I treated the same topic in a discourse delivered before the Architectural Association. About the same time I was trying experiments on the north front of Westminster Palace. A little later on, about 1865, I dealt with distemper paintings in Cirencester parish church and elsewhere. Waterproofing stone with paraffin wax, driven in by heat, was the subject of several trials in the later sixties. Afterwards the great fresco by G. F. Watts, in Lincoln's Inn Hall, was cleaned and repaired. This was in 1890. To the list may be added the works of Ford Madox Brown, in Manchester Town Hall, and other pictures and other buildings in various parts of the country, besides the long series of mural paintings in Westminster Palace.

I shall be glad if I have said anything to-night which will prove helpful in the preservation of mural paintings and the stonework in towns, especially in the case of historic buildings. The materials recommended are accessible, cheap, and easily applied. Doubtless there are other preparations available for the same purpose. Some of these may meet those conditions to which the materials I have recommended are not applicable.

NOTICES OF BOOKS.

Paper Technology. By R. W. SINDALL, F.C.S. London: Charles Griffin and Co., Ltd. 1906.

STUDENTS attending technical classes on the manufacture of paper will find this book a great help to them when revising their lecture work. While highly technical matter is omitted, a very readable account is given of the making of paper, and methods of determining its physical and chemical properties, which both paper-makers and users will find full of interesting matter. The determination of the chemical constituents of paper is discussed fully enough to enable the reader to get an elementary idea of the basis of the methods generally adopted, and the use of the microscope in the examination of paper is also explained. A useful glossary of trade terms will be appreciated by students, and the plates showing the fibres of different materials are a valuable addition to the book.

Solubilities of Inorganic and Organic Substances. By ATHERTON SEIDELL, Ph.D. New York: D. van Nostrand Company. London: Crosby Lockwood and Son. 1907.

THIS handbook of the quantitative determinations of the solubilities of all classes of substances is a valuable compilation. In all cases the author has referred to the original sources for his figures, in order to eliminate errors of quotation which might have crept into text-books, and in most cases he gives full references to his authorities, so that it would be an easy matter to look them up for experimental details if required. Moreover, in cases in which there are considerable discrepancies between the results of different investigators, an attempt has been made either by graphical methods, or else from theoretical or experimental considerations, to decide which results are probably more accurate, and these alone are tabulated in the book, which gives an admirably full and conveniently arranged list of solubilities in water and other solvents.

Radioaktive Umwandlungen. ("Radio-active Transformations"). By E. RUTHERFORD. Translated by M. LEVIN. Braunschweig: Friedrich Vieweg und Sohn. 1907.

THIS book is a translation of the Silliman Foundation lectures delivered by Prof. Rutherford at Yale University in March, 1905. The subject chosen for the lectures was the transformations of radio-active matter, and some account was also given of the general phenomena of radio-activity. Since the lectures were delivered many important discoveries have been made relating to radio-active changes, and the author has as far as possible brought the work up-to-date by additions and alterations. The translation has been done excellently, and Dr. Levin himself has in some cases added explanatory notes.

Die Chemische Analyse. ("Chemical Analysis"). Edited by Dr. B. M. MARGOSCHES. Vols. I. and II. Stuttgart: Ferdinand Enke. 1907.

THIS treatise on analytical chemistry, in which completeness is, above all things, aimed at, is to be issued in the form of monographs of convenient size. The author of each monograph will endeavour especially to give a comprehensive view of the branch of the subject entrusted to him, and the theory of analytical chemistry will be discussed, as well as the practice, in certain volumes of the series. The first volume contains a systematic account of the use of hydrazine in analysis, and has been written by Dr. Julius Schmidt. The uses of hydrazine and its salts in quantitative and qualitative work are first discussed, and then phenylhydrazine and its substitution products, and some other important derivatives of the parent substance are treated similarly. Special stress is laid upon the use of hydrazine in inorganic analysis, a use which is constantly being extended. The second volume by Dipl.-Ing. H. Nissenson is devoted to the determination of zinc, chiefly in ores of technical importance. Great prominence is given to the four methods, which were reported to give equally satisfactory results by the commission appointed to investigate the question, at the Sixth International Congress of Applied Chemistry at Rome, namely, Schaffner's process, Galetti's with potassium ferrocyanade, the gravimetric sulphuretted hydrogen method, and electrolysis, while other methods are also considered. Separation processes are included, and the monograph thus gives a full account of practically all reliable and convenient methods of estimating zinc.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

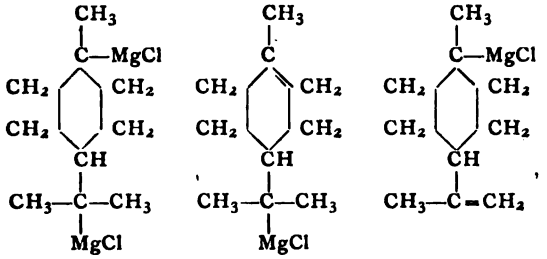
Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlv., No. 4, July 22, 1907.

Mixed Anhydride of Sulphuric and Nitric Acids.—Amé Pictet and Georges Karl.—Nitric anhydride dissolves in freshly distilled sulphuric anhydride with evolution of heat. When the product is distilled a thick liquid passes over between 218° and 220°. This liquid solidifies to a white crystalline mass on cooling; its melting-point is 124—125°. The same substance is obtained when solutions of the anhydrides are made separately in carbon tetrachloride and the two solutions are then mixed. The compound is very hygroscopic and fumes in air. It dissolves in water, evolving much heat, and giving a mixture of sulphuric and nitric acids. Analysis shows that the formula is $(SO_3)_4N_2O_5$, and hence it is probably a nitrosyl-tetrasulphate, $O<\begin{matrix}SO_2—O—SO_2—O—NO_2\\SO_2—O—SO_2—O—NO_2\end{matrix}$. The analysis

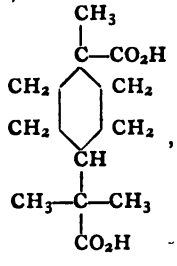
was performed by dissolving a known weight of the substance in water, determining the sulphur as barium sulphate, the nitrogen by Kjeldahl's method, and the total acidity by titration. When this substance is allowed to act upon organic compounds, complex products are formed, the nitration being accompanied by sulphonation, by oxidation, and by carbonisation. The authors have not succeeded in finding any liquid in which the mixed anhydride dissolves without attacking it.

Compounds of Nickel and Cobalt with Boron.—Binet du Jassonneix.—If mixtures of nickel or cobalt and boron are heated to 1100° or 1200° in a current of hydrogen, products are obtained which in their properties and structure recall the corresponding compounds of iron. The cobalt product, which contains about 5 per cent of boron, is attacked very slowly by warm hydrochloric acid. The residue then left contains 8·5 per cent of boron, and consists of the compound Co_2B. The corresponding nickel product does not yield a definite boride when treated with hydrochloric acid. If an ingot of the melt is used as anode in a solution of nickel chloride and a current is passed, the anode rapidly yields a metallic powder with composition corresponding to the formula Ni_2B. When the amount of boron exceeds 20 per cent, products are obtained which are more fusible than those which contain iron. The highest percentage of boron reached in these compounds is 27·1 and 27·2 respectively, corresponding to CoB_2 and NiB_2.

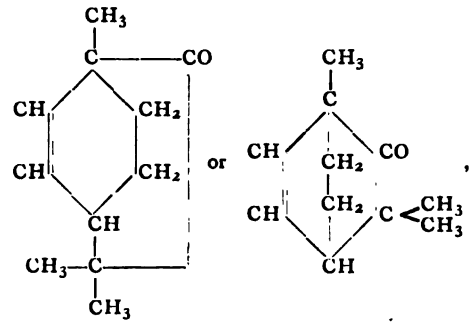
Menthane 1 . 8-Dicarboxylic Acid. A New Bicyclic Ketone.—Ph. Barbier and V. Grignard.—The action of powdered magnesium upon an ethereal solution of dipentene dichlorhydrate gives one dimagnesium and two monomagnesium compounds of formulæ—



and at the same time a hydrocarbon is formed, which appears to be dipentene. When carbon dioxide acts upon the mixture of magnesium compounds and water is added, one dibasic and two monobasic isomeric acids are formed. The first is easily separated by shaking the ethereal solution of the free acids and the hydrocarbon with sodium bicarbonate, while the monobasic acids can be extracted by the action of dilute soda. The dibasic acid is menthane 1 . 8-dicarboxylic acid,—



which can exist in two forms, both of which the authors have isolated. The *cis*-acid loses water when boiled with acetic anhydride, giving the anhydride $C_{10}H_{18}<^{CO}_{CO}>O$, which yields a viscous product when it is subjected to distillation under atmospheric pressure. From this viscous product a ketonic liquid with the formula $C_{11}H_{16}O$ separates on rectification *in vacuo*. Thus, the decomposition of the anhydride proceeds as follows:— $C_{10}H_{18}<^{CO}_{CO}>O = CO_2 + H_2 + C_{11}H_{16}O$. The new ketone may be represented by the formula—



and it is thus 1 . 3 . 3-trimethyl-1 . 7 . 8 . 4-bicyclo-5 . 2-hexanone.

New Silicide of Platinum.—P. Lebeau and A. Novitzky.—At a bright red heat a mixture of finely-divided silicon and platinum yields a compound, much heat being evolved, so that the incandescence of the mass visibly increases. Finally, an ingot looking like silicon is obtained, the polished surface of which reveals distinctly the existence of two homogeneous substances. One of these is silicon, and by the action of dilute potash the other constituent can readily be extracted. Its analysis gives the formula SiPt. This compound can be obtained in the crystalline state, and in its chemical properties it closely resembles platinum. It fuses, however, much more readily than platinum, its melting-point being about 1100°. It dissolves completely in aqua regia, and is more readily attacked by oxidising agents than platinum is.

General Method of Preparing Anhydrous Metallic Borides from Oxides.—F. Bourion.—At a temperature below a red heat hydrobromic acid converts oxides which are easy to reduce, such as those of nickel and cobalt, into anhydrous bromides, and also the oxides of the rare earths. The preparation is rendered easier if small quantities of sulphur chloride are added to the acid. This chloride is totally converted into bromide, and acts as a diluent to the acid and effects the conversion of the whole of the oxide into bromide; when hydrobromic acid alone is passed rapidly over the hot oxide the transformation is incomplete owing to the pastiness of the mass. Moreover, the sulphur bromide reacts on the water-vapour formed and regenerates hydrobromic acid, and the rate of the reaction is increased. The sulphur chloride must be heated to between 60° and 90°. The bromides thus prepared from oxides include the following compounds:—$ThBr_4$, $CrBr_3$, $NiBr_2$, $CoBr_2$, $NdBr_3$, $CeBr_3$, $ThOBr_2$, $LaBr_3$, $SmBr_3$, $PrBr_3$, $GdBr_3$, $DyBr_3$, $YtBr_3$, $TbBr_3$; the last eight compounds being obtained for the first time.

MISCELLANEOUS.

German Colonial Society Prize.—The President of the German Colonial Society offers a prize of £150 for a method to produce an extract from mangrove bark that will impart as light a colour as possible to leather and will only slightly darken by exposure to light. The mangrove bark contains a large amount of tannin and also a red colouring matter that prevents the bark and its extract from successfully competing with other tanning agents. The problem to be solved is the practical removal of this red colour. Competitors are invited to send in their methods by July 20, 1908, to Deutsche Kolonialgesellschaft, Schellingstrasse 4, Berlin.—*Chemist and Druggist.*

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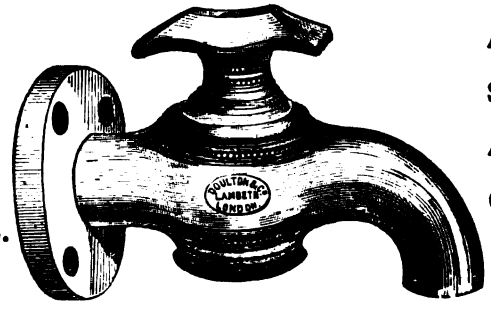

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This Laboratory was founded by Dr. LUDWIG MOND, F.R.S., as a Memorial of Davy and Faraday, for the purpose of promoting, by original research, the development and extension of Chemical and Physical Science.

MICHAELMAS TERM.—Monday, October 7, to Saturday, December 14.
LENT TERM.—Monday, January 6, to Saturday, April 11.
EASTER TERM.—Monday, May 4, to Saturday, July 25.

Full information and forms of application can be had from the Assistant Secretary, Royal Institution, Albemarle Street, W.

To prevent delay, Candidates ought to send in their applications for admission during the course of the Term preceding that in which they wish to enter.

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BOTANY	V. H. BLACKMAN, M.A.
ZOOLOGY	H. W. UNTHANK, B.A., B.Sc.
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Metallurgy	Prof. A. HUMBOLDT SEXTON, F.C.S., F.I.C.

The Courses of Instruction in these Departments are arranged for Students preparing to become Manufacturing or Analytical Chemists, Metallurgists, or Science Teachers. The Courses in Chemistry qualify for the Examinations of the Institute of Chemistry, and of the Universities of Glasgow, Edinburgh, and London.

SESSION 1907-8 begins on MONDAY, SEPTEMBER 23, in the New Buildings recently erected for the College. The ENTRANCE EXAMINATION begins on MONDAY, SEPTEMBER 16.

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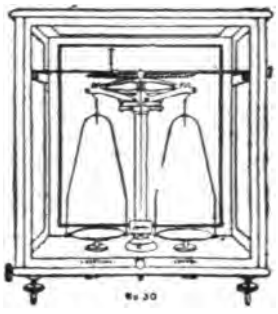

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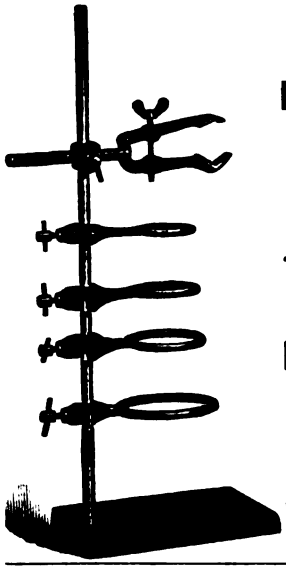

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THE CHEMICAL NEWS.
Vol. XCVI., No. 2493.

(STUDENTS' NUMBER).

UNIVERSITIES AND COLLEGES.

UNIVERSITY OF LONDON.

Candidates for any Degree in this University must either have passed the Matriculation Examination in this University, or be admitted under the Statute which provides that the Senate may admit graduates of or persons who have passed the examinations required for a degree in other Universities approved by it. This and all other Examinations of the University, together with the Prizes, Exhibitions, Scholarships, &c., are open to Women upon exactly the same conditions as to Men.

There are three Examinations for Matriculation in each year; commencing on the second Monday in September, January, and June (or July, as may hereafter be determined).

Every candidate entering for the Matriculation Examination must pay a Fee of £2. If a candidate withdraws his name, or fails to present himself at the Examination, or fails to pass it, the Fee shall not be returned to him.

Candidates are not approved by the Examiners unless they have shown a competent knowledge in each of the following five subjects:—(1) English—Composition, Précis Writing, salient facts in English History and Geography. (2) Elementary Mathematics. (3) Latin or Elementary Mechanics, or Elementary Physics—Heat, Light, and Sound, or Elementary Chemistry, or Elementary Botany. (4) and (5) Two of the following subjects, neither of which has already been taken under Section (3). If Latin be not taken, one of the other subjects selected must be another Language from the List, either ancient or modern:—Latin, Greek, French, German, *Arabic, *Sanskrit, *Spanish, *Portuguese, *Italian, *Hebrew, and *Zoology, Ancient History, Modern History, Logic, Physical and General Geography, Geometrical and Mechanical Drawing, Mathematics (more advanced), Elementary Mechanics, Elementary Chemistry, Elementary Physics—Heat, Light, and Sound, Elementary Physics—Electricity and Magnetism, and Botany. Candidates in subjects marked with asterisk must give at least two months' notice before the commencement of the Examination.

A Pass Certificate, signed by the Principal, will be delivered to each successful candidate after the Report of the Examiners has been approved by the Senate.

Several valuable Scholarships and Exhibitions are available to students.

Intermediate Examination in Science.

The Intermediate Examination in Science will commence on the second Monday in July.

No candidate (with the exception of such as have obtained Honours at the Matriculation Examination in the preceding January) is admitted to this Examination within one academical year of the time of his passing the Matriculation Examination.

The Fee for this Examination is £5.

Examination for Honours.

Candidates for Honours in Chemistry will be examined in Inorganic Chemistry, treated more fully than in the Pass Examination. This Examination will consist of two printed papers and a practical examination.

In the Examination for Honours, the Candidate, not being more than 22 years of age at the commencement of the Pass Examination, who most distinguishes himself will receive an Exhibition of £40 per annum for the next two years.

B.Sc. Examination.

The B.Sc. Examination will be held on the fourth Monday in October.

Candidates for this Examination are required to have passed the Intermediate Examination in Science at least one academical year previously, and to have passed the Matriculation Examination at least three years previously.

The Fee for this Examination is £5.

Examination for Honours.

For the examination for Honours in Chemistry candidates are required to show a general acquaintance with General Theoretical Chemistry, Chemistry of Carbon Compounds, Physical Chemistry, and History of Chemistry since the time of Boyle.

The candidate, being not more than 23 years of age, who most distinguishes himself in Chemistry, will receive £50 per annum for the next two years, with the style of University Scholar.

Doctor of Science.

The examination for the Degree of Doctor of Science takes place annually within the first twenty-one days of June.

No candidate is admitted to the examination for the Degree of D.Sc. until after the expiration of two Academical Years from the time of his obtaining the Degree of B.Sc. in this University.

Preliminary Scientific (M.B.) Examination.

This Examination takes place twice in each year,—once, for Pass and Honours, commencing on the second Monday in July; and once for Pass Candidates only, commencing on the third Monday in January.

The Fee for this examination is Five Pounds.

UNIVERSITY OF OXFORD.

Waynflete Professor of Chemistry—W. Odling, F.R.S.
Lees Reader in Chemistry—G. Brereton Baker, M.A.

Every Student must reside in one or other of the Colleges or Halls, or in licensed lodgings, for a period of three years. Students of Chemistry can obtain the degree of B.A. by passing preliminary examinations in Arts and in Science, and a final Honour examination in Chemistry. Chemistry may also be taken as part of the examination for a Pass degree. Graduates of other Universities suitably qualified can obtain the degree of Bachelor of Science after an approved course of study or research and two years' residence.

University Laboratory.—Demonstrators, W. W. Fisher, M.A., J. Watts, M.A., and J. E. Marsh, M.A.—The fee for students working in the Laboratory for three days in the week during the Term is £3; for students working every day, £5.

Scholarships of about the value of £80 are obtainable at the majority of the colleges, by competitive examination in Natural Science.

More detailed information may be obtained from the Examination Statutes; the Student's Handbook to the University; and from the professors and college tutors.

UNIVERSITY OF CAMBRIDGE.

Professor of Chemistry—G. D. Liveing, M.A., F.R.S.
Jacksonian Professor of Natural and Experimental Philosophy—Sir James Dewar, M.A., F.R.S.

The Student must enter at one of the Colleges or Hostels, or as a Non-collegiate Student, and keep terms for three years by residence in the University. He must pass the previous examination in Classics and Mathematics, which may be done in any term of residence or before commencing residence. He may then proceed to take a Degree in Arts, either continuing mathematical and classical study, and passing the ordinary examinations for B.A., or going out in one of the Honour Triposes.

A graduate of another University may be admitted as an "advanced" student, and obtain a degree after two years' residence in the University.

The scholarships, ranging in value from £20 to £100 a year, are chiefly given for mathematical and classical proficiency. Scholarships, or Exhibitions, are given for Natural Science at the several Colleges; the dates of the examinations vary, but are always fully advertised.

The Chemical Laboratory of the University is open daily for the use of the Students. The Demonstrators attend daily to give instruction. A list of the lectures is published annually, in June, in a special number of the *Cambridge University Reporter*, which may be had from the Cambridge Warehouse, in Paternoster Row, or through any bookseller.

Non-collegiate Students are allowed to attend certain of the College Lectures and all the Professors' Lectures, and have the same University status and privileges as the other Students. Full particulars may be obtained by forwarding a stamped directed envelope to the Assistant Registrary, Cambridge, or from the *Cambridge University Calendar.*

UNIVERSITY OF DUBLIN.

TRINITY COLLEGE.

Professor of Chemistry—Sydney Young, D.Sc., F.R.S.

Professor of Applied Chemistry—Emil A. Werner, F.C.S., F.I.C.

Demonstrator—W. C. Ramsden, F.C S.

Junior Demonstrator—W. R. G. Atkins, B.A.

The general Quantitative and Research Laboratories include working accommodation for about 130 Students The Laboratories will open on October 1st. Lectures will commence about November 1st.

The Laboratories and the Lectures ofthe Professor of Chemistry can be attended by Students who do not desire to reside in the University or proceed to its Degrees.

The full Course of General and Analytical Chemistry occupies three years, but a Student is free in his third year to devote most of his time to a special department of Pure or Technical Chemistry. Students can enter for any portion of the Course. The Lectures delivered are:—

1. *Inorganic Chemistry and Chemical Philosophy.*—Elementary, first year; Advanced Inorganic Chemistry, second year; Physical Chemistry, third year.
2. *Organic Chemistry.*—General, second year; advanced, third year.
3. *Metallurgy.*—A Course for Engineering and Technical Students.
4. *Agricultural Chemistry.*—Theoretical and Practical Courses.

The Laboratories are open every day from 10 to 5 o'clock (except Saturdays, when they close at 1 o'clock).

The Summer Course of Practical Chemistry for Medical Students begins early in April and terminates about the end of June.

A special course for Dental Students will be given.

The University of Dublin grants the Degree of Doctor of Science to graduates of Master's standing whose independent researches in any branch of Science are of sufficient merit.

By recent decrees, Prizes in Chemistry and Physics will be given in future at the October (Arts) Entrance Examination, and also at the Terminal Examinations of the Junior and Senior Freshmen Years.

Similarly, two Science Scholarships will be obtainable by Undergraduates, and tenable for five years. These Foundation Scholars receive £20 per annum, have free commons, their chambers for half the charge paid by other students, and their tutorial fees are at one-fourth the usual rates.

KING'S COLLEGE.

(DIVISION OF ENGINEERING AND APPLIED SCIENCE).

Senior Professor of Chemistry—J. M. Thomson, LL.D. F.R.S.

Professor—Herbert Jackson, F.C.S.

Lecturer and Demonstrators—P. H. Kirkaldy, F.C.S., D. Northall Laurie, F.C.S., S. W. Collins, and L. Hinkel.

The Academical Year consists of Three terms. The days fixed for the Admission of New Students in the Academical Year 1907-1908 are Oct. 2, Jan. 8, and April 29.

Students of the First Year are admitted to the Course of Theoretical and Applied Chemistry. The Course commences with a view of the conditions suitable for the production of Chemical Phenomena, after which the laws of Chemical Attraction are discussed, and the Non-metallic Elements and their principal compounds are described. The Metals and their principal compounds are next examined, care being taken to point out the applications of the Science to the Arts; and the processes of the different Manufactures and of Domestic Economy are explained and illustrated. Examinations of the Class, both *vivâ voce* and by written papers, are held at intervals during the course at the usual Lecture hour.

Second Year.—Students attend in the Laboratory twice a week, and they go through a course of Chemical Analysis, both by liquid tests and the blowpipe, analysis of ores, liquids, &c., and Elementary Volumetric Analysis.

Experimental and Analytical Chemistry in the Laboratory.—The object of this Class is to afford to Students who are desirous of acquiring a knowledge of analysis, or of prosecuting original research, an opportunity of doing so under the superintendence of the Professor and Demonstrator; Students may enter, upon payment of extra fees, at any time except during the vacation, and for a period of one, three, six, or nine months, as may best suit their convenience. The laboratory hours are from ten till four daily, except Saturday.

In addition to the Laboratory Fee, each Student defrays the expenses of his own experiments. The amount of this expense, which is comparatively trifling, is entirely under his own control.

Fees.—Chemistry: Winter Session, £5 5s.; Summer Session, £3 3s. Practical Chemistry: Winter Session, £8 8s.; Summer Session, £4 4s. Experimental and Analytical Chemistry—Five days a week: One month, £4 4s.; One Term, £10 10s.; Two Terms, £18 18s.; Three Terms, £26 5s. Three days a week: One month, £2 12s. 6d.; One Term, £6 6s.; Two Terms, £11 11s.; Three Terms, £15 15s.

For fuller details the separate Syllabuses provided for each class should be consulted.

METALLURGY.

Professor—A. K. Huntington, A.R.S.M, F.I.C., &c.

The following subjects are treated of in the Lectures: The Selection and Economic Preparation of Fuel and of Refractory Materials; the methods by which metals are obtained from their ores, and the means by which they are rendered suitable for the various requirements of the Arts.

Particular attention is paid to the study of the Nature and Properties of Metals and Alloys available for Constructive Purposes.

In the Metallurgical Laboratory, which is always open during College hours, the relation between the Chemical Composition of Metals and their Mechanical Properties may be studied by the aid of Testing Machinery.

Fee, £3 3s. for the Course.

PHOTOGRAPHY.

Lecturer—Prof. J. M. Thomson, LL.D., F.R.S.

For particulars apply to Prof. Thomson.

EVENING CLASSES.

Classes for Evening Instruction in various subjects are held during the Winter Session.

UNIVERSITY COLLEGE.

FACULTY OF SCIENCE.

Professors—Sir William Ramsay, K.C.B., LL.D., F.R.S. (Inorganic and Physical Chemistry); J. Norman Collie, Ph.D., F.R.S. (Organic Chemistry).

Assistants—E. C. C. Baly, F.I.C.; N. T. M. Wilsmore, M.Sc.; Kathleen Burke, B.Sc.; R. W. Gray, Ph.D.; and S. Smiles. D.Sc.

The Session is divided into three Terms, as follows:—First Term, from October 1 to December 20; Second Term, from January 14 to March 27; Third Term, from April 28 to July 8.

Introductory Course of Inorganic Chemistry.

Tuesday and Thursday, at 9. Practical, Thursday, 2 to 3.30, or 3.30 to 5. Fee, £10 10s.

This Course treats of the chief physical and chemical

characters of the Non-metallic Elements, their preparation and characteristic tests.

Junior Course of Inorganic Chemistry.

First and Second Terms: The Class meets four times a week, on Mondays, Wednesdays, Fridays, and Saturdays, at 9, for Lectures, Examinations, and Exercises.

In this Course the physical principles bearing on Chemistry are first discussed, and the Chemistry of the Elements and their compounds is treated in considerable detail, under the headings—Elements; hydrides, halides, oxides, sulphides, &c., borides, carbides and silicides, nitrides, phosphides, &c., and alloys. Special attention is devoted to substances of commercial importance. The concluding Lectures are devoted to Physical Methods and their bearing on Chemical Problems.

Third Term: Lectures will be given on Mondays and Fridays at 9 and on Wednesdays at 11, on the chief types of Carbon Compounds.

Fees: Course, £7 7s.; First or Second Terms, £4 4s.

A Practical Class will meet throughout the Session.

Course of Physical Chemistry.

October to February: Tuesday and Thursday at 9. February to June: Monday and Saturday at 9.

The Principles of Chemistry will be specially considered, comprising the Atomic Theory, Chemical Classification, the Periodic Law, Thermal Chemistry, Dissociation, the Application of Physical Methods to the Solution of Chemical Problems, and the influence of Mass and Temperature on the progress of Reactions. Special attention is paid to the most recent Chemical Theory researches.

Fees:—Courses £5 5s.; Term, £2 2s.; for a second course, £1 1s.

Senior Course of Inorganic Chemistry.

This Course will begin about the middle of February; Tuesday and Thursday at 9. Fee, £3 3s.

Electro-chemistry.

First Term, Monday and Saturday at 9. Fee, £1 1s.

Organic Chemistry.

Mon. at 12, Wed. and Fri. at 9, during the session.

This Course is suitable for Students who intend to study Chemistry from a scientific standpoint. No previous knowledge of Organic Chemistry is expected of those attending the Class, which should, however, be taken concurrently with the Course of Physical Chemistry, and with Practical Organic Chemistry in the Laboratory.

Fee:—For the Course, £6 6s.; for a Term, £2 12s. 6d.; for a Second Course, £3 3s.

An Advanced Course will be held twice a week throughout the Session for those engaged in prosecuting research in Organic Chemistry. Fee, £5 5s.; Term, £2 2s.

Practical Classes.

Practical Classes in Inorganic and Organic Chemistry are conducted by the Assistants.

Laboratories of General and of Organic Chemistry.

The Laboratories are open daily from 9 a.m. to 5 p.m., Saturdays excepted, from October until the middle of July, with a short recess at Christmas and at Easter.

Fees: for the Session, £26 5s.; six months, £18 18s.; three months, £10 10s.; one month, £4 4s.

Three specified days a week:—for the Session, £15 15s.; six months, £11 11s.; three months, £6 6s.; one month, £2 12s. 6d., exclusive of expense of materials. Students may enter at any period of the Session.

When accompanied by, or preceded by, attendance on the Lectures on Inorganic and Organic Chemistry, the Laboratory Courses qualify Students in the application of Chemistry to Manufactures, Metallurgy, Medicine, or Agriculture, &c.

There is also a Chemical Library containing the chief Journals and Standard Works on Chemistry.

Certificates of Honour are granted to competent Students on the work done during the Session. Several valuable Scholarships are available to students.

ROYAL COLLEGE OF SCIENCE AND ROYAL SCHOOL OF MINES.

Professor of Chemistry—W. A. Tilden, D.Sc., F.R.S.

Assistant Professor—M. O. Forster, Ph.D., D.Sc.

Demonstrators—H. Chapman Jones; G. T. Morgan, D.Sc., A.R.C.S.; and J. C. Philip, M.A., Ph.D., B.Sc.

Assistants—G. S. Newth and Miss Whiteley, D.Sc., A.R.C.S.

The Royal College of Science at South Kensington is intended, primarily, for the instruction of teachers, and of students of the industrial classes selected by competition in the examinations of the Board of Education. The Royal School of Mines is incorporated with the Royal College of Science. Students entering for the Associateship of the Royal School of Mines obtain their general scientific training in the Royal College of Science. The instruction in the Royal College of Science is arranged in such a manner as to give the Students a thorough training in the general principles of Science, followed by advanced instruction in one or more special branches of Science. The Associateship is granted in certain divisions or lines of study. Students who go through any one of the prescribed courses of instruction and pass the necessary Examinations receive a Certificate of Associateship of the Royal College of Science, or of the Royal School of Mines. Students who are not candidates for the Associateship are permitted to enter as occasional students in one or more special branches of science. The Associateship of the Royal College of Science is given in one or more of the following divisions:—Mechanics, Physics, Chemistry, Biology, and Geology, and the Associateship of the Royal School of Mines in Metallurgy and Mining.

The course of instruction lasts for three years, is the same for all the divisions during the first year, after which it is specialised according to the particular division in which the student is working for the Associateship.

Examinations are held at the end of each course of instruction and at such other periods as may be found necessary. On the results of these examinations the successful candidates are arranged in two classes, first and second. There are also "Honours" examinations for the subjects of the third year, the successful candidates being placed in order of merit. A student obtains the Associateship who passes in all the subjects of the first year, and, in the second and third year, those subjects prescribed as necessary for the division in which he seeks to obtain his Associateship. A student who goes through the prescribed course of instruction in any subject except Mining and Metallurgy and passes the necessary examinations receives a certificate to that effect.

Students who do not wish to attend the lectures are admitted for short periods to the laboratories, at the discretion of the Professors. The fees for the laboratories are £4 per month.

Students not entering for the Associateship are admitted to any particular course of study, so far as there is room, on payment of the fees shown in the following table:—

	Lectures.	Laboratory.
	£	£
Chemistry	3	13
Physics	5	12
Biology with Botany	5	12
Geology with Mineralogy ..	4	8
Mechanics	4	6
Metallurgy	2	13
Mining	4	

The fee for the course of Mine Surveying is £10.

The fees for the first two years amount to about £75, and for the remainder of the course for the Associateship they vary from £30 to £40.

The Session is divided into two Terms. The first Term begins about the first week of October, and ends about the middle of February. The second Term begins in the middle of February, and ends about the middle of June.

The hours of study are from 10 a.m. to 1.15, and from

2 to 4 or 5 p.m. every day, except on Wednesday and Saturday, when the College closes at 1 p.m.

Several valuable Exhibitions, Scholarships, and Prizes are attached to the studentship.

Summer Courses for Teachers.—Short courses of instruction are given annually, about July, in different branches of science for the benefit of teachers of science schools in the country. The courses last three weeks. About 250 teachers are admitted to them, and they receive third class railway fare to and from South Kensington, and a sum not exceeding £3 towards their expenses.

THE SCHOOL OF PHARMACY OF THE PHARMACEUTICAL SOCIETY OF GREAT BRITAIN.

The Sixty-fifth Session will commence on Oct. 1, 1907.

Professors—Chemistry, Arthur W. Crossley, D.Sc., Ph.D., F.I.C., F.R.S., (Dean); Botany (vacant); Pharmaceutics, Henry G. Greenish, F.I.C., F.L.S.

A Course of Lectures on Physical, Inorganic, and Elementary Organic Chemistry commences in October and terminates at the end of June. An Advanced Course of Lectures begins in October and extends to the end of March. These Lectures are adapted to the requirements of Pharmaceutical and Medical Students, and also of those who are proceeding to degrees at the University of London, or who are preparing for the examinations of the Institute of Chemistry.

Entries may be made for single classes. Certificates of attendance at the two Courses of Lectures on Chemistry and at the Chemical Laboratories are accepted as evidence of chemical training by the Institute of Chemistry in connection with the Examinations for the Associateship, and also by the conjoint Board of the Royal Colleges of Physicians and Surgeons, as well as by other examining bodies.

Prospectuses and further information may be obtained from the Dean of the School, 17, Bloomsbury Square, London, W.C.

UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH.

UNIVERSITY OF WALES.

Director of the Edward Davies Chemical Laboratories and Professor—J. J. Sudborough, D.Sc. (Lond.), Ph.D. (Heidelberg), F.I.C.

Assistant Lecturers and Demonstrators—A. Brooke, Ph.D. (Strass.), and T. C. James, M.A. (Cantab.), B.Sc.

Lecturer in Agricultural Chemistry—J. Jones Griffith, B.Sc. (Wales).

The College is open to men and women students above the age of sixteen years. The Session commences on Oct. 1st, on which day all Students will be expected to meet the Professors in the Examination Hall of the College.

Lecture Courses.—(1) Intermediate Science Course; four lectures weekly throughout the Session. (2 and 3) B.Sc. Courses; A, three lectures weekly on Organic Chemistry; B, three lectures weekly on General and Physical Chemistry. (Courses A and B will generally be given in alternate Sessions; for 1907-1908, Course A). (4 and 5) Courses in Agricultural Chemistry. For students in their first year, 3 lectures, and for those in their 2nd year, 2 lectures weekly during the Michaelmas and Lent terms.

Laboratory Courses.—The Laboratories are open daily from 9 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays. Regular Courses of practical work, suitable for the B.Sc. degree of the Universities of London and Wales, or for the Associateship of the Institute of Chemistry, can be followed. Facilities are given for Students wishing to undertake research work. Special Courses will be arranged for those who intend to follow Medicine or Pharmacy, or any one particular branch of Applied Chemistry, always provided that such Students possess the requisite knowledge of Theoretical Chemistry. The hours will be arranged, as far as possible, to suit the requirements of the individual Student.

The College is recognised by the University of Edinburgh and the Royal University of Ireland, and by the Colleges of Physicians and Surgeons of England, Scotland, and Ireland as an institution at which the instruction necessary for their respective Diplomas in Medicine, in Chemistry, Physics, and Biology may be given. One year for graduation in Medicine and two years for graduation in Science may be spent at Aberystwyth.

Fees.—The Fee for the whole Session, if paid in advance, is £10; if paid by Single Terms, for the first term of attendance in each Session, £4; for the second term, £3 10s.; for the third term, £3. These composition fees enable the Student to attend any or all the Classes of the College, with the exception that a small extra fee is charged for Laboratory Instruction. Thus, for Practical Chemistry, the additional fee is, for six hours' work per week, 12s. 6d. per term, and for twelve hours, 25s. per term. The fees for those who desire to spend several days weekly in the laboratory may be learned on application to the Registrar. Fee for a single Lecture Course £1 per term.

Scholarships and Exhibitions varying in value from £10 to £40 per annum will be offered for competition at examinations which commence on September 18, and exhibitions are awarded at the end of the Session on the results of the class examinations.

Intending Students requiring further information are recommended to write to the Registrar for a copy either of the General Prospectus or of one of the Special Prospectuses issued for the Agricultural and Normal Departments.

UNIVERSITY COLLEGE OF NORTH WALES, BANGOR.

A CONSTITUENT COLLEGE OF THE UNIVERSITY OF WALES.

Chemistry.—Professor, K. J. P. Orton, M.A., Ph.D., F.I.C. Assistant Lecturer and Demonstrator, Alice E. Smith, B.Sc. Assistant Lecturer in Agricultural Chemistry, Alan Baguley, B.Sc., F.I.C. Junior Demonstrator, J. O. Hughes, B.Sc.

Physics.—Professor, E. Taylor Jones, D.Sc.

The Session opens October 3rd, 1907. All regular classes are open to men and women students above the age of 16 years. The following Courses of Lectures will be given.

Matriculation Course.—Subjects: Those prescribed for the Matriculation Examination of the University of Wales. Fee for the Session £3 3s.

Intermediate Course.—Inorganic Chemistry and Elementary Physical Chemistry. Fee for the Session, £3 13s. 6d.

B.Sc. Course.—Inorganic and Physical Chemistry. Fee for the Session, £3 3s.

Agricultural Chemistry.—Fee, £2 2s.

Laboratory Courses.—The laboratory is open on five days of the week from 10 a.m. to 5 p.m. for instruction in Chemical Analysis and in the Application of Chemistry to Medicine and the Industrial Arts. Fees: six hours per week, £1 1s. per Term; twelve hours, £2 2s.; eighteen hours, £3 3s. Composition Fee for all Laboratory Classes of the Intermediate Science Course taken in one year, £4 4s.

The Chemistry, Botany, Zoology, and Physics Courses are recognised for Medical graduation in the Universities of Edinburgh and Glasgow, and students can make one *Annus medicus* at the college. Students are prepared for the First Examination of the Conjoint Board of the Royal Colleges of Surgeons and Physicians. The Science Courses are recognised for part of the science degree course of the University of Edinburgh.

UNIVERSITY COLLEGE OF SOUTH WALES AND MONMOUTHSHIRE, CARDIFF.

Professor—C. M. Thompson, M.A., D.Sc., F.C.S.
Assistant Professor—E. P. Perman, D.Sc., F.C.S.
Demonstrator—R. D. Abell, D.Sc.
Lecturer in Metallurgy—A. A. Read, F.I.C., F.C.S.

The Session commences October 8th, and terminates on June 26th, and is divided into three terms.

The Junior Course (delivered during the Michaelmas term only) consists of about 50 lectures, and will cover the subjects prescribed for the Matriculation examinations of the University of Wales and the University of London. Fee, £2 2s. A revision class is held in the Summer term.

The Intermediate Course consists of about 80 lectures held during the Lent and Summer terms in continuation of the Junior Course; together with laboratory practice it forms the qualifying course for the Intermediate Examination of the University of Wales, and will cover the subjects required for the Intermediate Examination in Science of the University of London. Fee, £4 4s.

The Senior Course consists of about 80 lectures on Organic Chemistry; Fee, £3 3s.

The following lectures on Metallurgy will be given by Mr. Read:—10 lectures on Fuel; Fee, 10s. 6d. 20 lectures on General Metallurgy; Fee, £1 1s. 30 lectures on the Manufacture of Iron and Steel; Fee, £1 1s. A practical course on Iron and Steel Analysis will also be held, and practical instruction in Dry Assaying will be given in the Metallurgical Laboratory, which is fitted with the necessary furnaces and apparatus.

In the laboratory each student works independently, so that the course of study may be adapted to the requirements of the individual. Hours, 9 to 1 and 2 to 5; Saturday, 9 to 1. Fees—Six hours per week, £2 2s. per term; twelve hours, £3 3s. per term; eighteen or more hours, £4 4s. per term.

Registered medical students can prepare for the Intermediate M.B. Examination of the University of London, and spend three out of their five years of medical study in Cardiff. Medical students wishing to graduate at a Scottish University, or preparing for a Conjoint Board Surgical and Medical Diploma, or for the Diploma of the Society of Apothecaries, can spend two years in Cardiff. For further information see the prospectus of the Faculty of Medicine, which may be obtained from the Registrar.

The College is recognised as an institution at which two years of the course for the degree of Bachelor of Science of the University of Edinburgh may be spent.

Students by making a payment of £10 at the commencement of each session may compound for all lecture fees for the whole session. Laboratory fees are not included in the composition fee, but Students preparing for the Science Examinations of the University of Wales and of the University of London may, by making a payment of £13 13s. at the commencement of each Session, compound for both Lecture and Laboratory Fees during the Session.

At the entrance examination in September, and the annual examination in June, several scholarships and exhibitions are awarded. Great importance is attached to special excellence in one subject.

The College Prospectus, and also further information as to scholarships, may be obtained from the Registrar.

A Hall of Residence for Women Students is attached to the College.

UNIVERSITY COLLEGE, BRISTOL.

Professor of Chemistry—Francis Francis, D.Sc., Ph.D., F.I.C.

Lecturer (Physical Chemistry)—James W. McBain, M.A.

Lecturer—Oliver C. M. Davis, B.Sc., F.I.C.

Lecture Assistant—J. H. Sturgess.

The session 1907-1908 will begin on October 1. Lectures and classes are held every day and evening throughout the Session. In the Chemical Department lectures and classes are given in all branches of theoretical chemistry, and instruction in practical chemistry is given daily in the chemical laboratory. A Laboratory has recently been fitted with a complete equipment for all ordinary measurements in Physical Chemistry. The department of experimental physics includes various courses of lectures arranged progressively, and practical instruction is given in the physical and electrical laboratories. The Department of Engineering and the Constructive Professions is designed to afford a thorough scientific education to students intending to become engineers, or to enter any of the allied professions, and to supplement the ordinary professional training by systematic technical teaching. This department includes courses specially arranged for students intending to become civil, mechanical, electrical, or mining engineers, surveyors, or architects. Those who attend the mechanical engineering course enter engineering works during the six summer months, and, in accordance with this scheme, various manufacturing engineers in the neighbourhood have consented to receive students of the College into their offices and workshops as articled pupils at reduced terms. Medical education is provided by the Faculty of Medicine of the College. Several Scholarships are tenable at the College. Full information may be obtained from the Registrar.

Day Lectures.

Inorganic Chemistry.

The Courses treat of the principles of Chemistry, and of the Chemistry of the Non-Metals and Metals.

Introductory Course.—Three Lectures a week will be given during the First and Second Terms, and at least one Lecture a week during the Third Term. Fee, £3 13s. 6d.

General Course.—Three Lectures a week will be given throughout the Session. Fee, £3 13s. 6d.

Systematic Physical Chemistry.—Two Lectures a week will be delivered throughout the Session. Fee, £3 13s. 6d.

Electro-chemistry.—One Lecture a week will be given during the Third Term. Fee, £1 1s.

Advanced Course.—Two Lectures a week will be given throughout the Session. Fee, £3 13s. 6d.

Organic Chemistry.

General Course—Three Lectures a week will be given throughout the Session. Fee, £3 13s. 6d. An advanced course of lectures will also be given one day a week during the session. Fee, £2 2s.

Colloquium.

A weekly Colloquium will be held by members of the Staff to discuss recent advances in the various departments of Chemistry. Students and others interested are invited to attend.

Practical Chemistry.—Laboratory Instruction.

The Chemical and Metallurgical Laboratories will be open daily from 9 a.m. to 5 p.m., except on Saturdays, when they are open to senior students only. Instruction will be given in the Laboratory in all branches of Practical Chemistry, including Qualitative and Quantitative Inorganic and Organic Analysis, the preparation of Chemical Products, Metallurgy, and Inorganic and Organic Research. Special facilities will be afforded to those who desire to study Practical Chemistry as applied to the different processes employed in the Arts and Manufactures. Fees in Guineas—

Days per Week ..	Five.	Four.	Three.	Two.	One.
Per Session	15	12½	10	7½	5
,, Two Terms ..	11	9	7½	5½	3½
,, One Term ..	7	6	4½	3½	2½

Students may arrange to divide their days of laboratory work into half-days. Special facilities are afforded for Research and Post-graduate work.

Chemical Scholarship.—Among others, a Chemical and a Metallurgical Scholarship each of £25 are offered for competition.

Evening Lectures.

A course of Lectures dealing with the principles and theories of modern Chemistry will be delivered during the First and Second Terms. Fee, 10s. 6d.

Practical Chemistry—Laboratory Instruction.—The Laboratory will be open one evening a week from 6 till 9. Instruction will be given in Qualitative and Quantitative Analysis, and in the Preparation of Chemical Products. Fees:—Two Terms, 21s; One Term, 12s. 6d.

University College, Bristol, has been approved by the Council of the Institute of Chemistry as a College at

which all the subjects required for the admission of Associates to the Institute are taught.

The Calendar of the College, price 1s. (post-free, 1s. 4d.), containing detailed information of the various Courses, may be obtained on application to the Registrar.

MERCHANT VENTURERS' TECHNICAL COLLEGE, BRISTOL.

CHEMISTRY.

Professor—J. Wertheimer, B.Sc., B.A., F.I.C., F.C.S.
Assistant Professor—Frederick W. Rixon, M.Sc., Ph.D.
Lecturers—H. A. M. Borland, A.R.C.S.; E. E. Elt, B.Sc.
Demonstrators—E. H. T. Parker; P. W. Alloway; C. D. Fuller.
Assistants in Chemical Laboratory—W. F. Phillips and C. Cox.

The Laboratories of this Department are open during the Term on every week-day as a School of Practical Chemistry and Analysis to Students of either sex. Each Student works independently, and receives individual instruction and help.

The training in this Department is intended to fit Students to become Professional Chemists, to prepare them for Medical or Pharmaceutical examinations in Chemistry, to instruct them in the branches of Applied Chemistry required in Manufactures and Agriculture.

Special facilities will be given to Students wishing to undertake research work approved by the Professor; and the Courses provide for the Examinations in Chemistry for the B.Sc., M.B., and D.Sc. degrees of the University of London.

The three years' course at this College in the subjects of Theoretical and Practical Chemistry, Theoretical and Practical Physics, and Elementary Mathematics, is accepted by the Council of the Institute of Chemistry as satisfactory evidence of the training of candidates for the Associateship of the Institute.

The Laboratories are open every week-day from 9.30 till 12.30, and from 2 to 5 p.m., except Saturday, when they close at 12.30.

The Annual Fee of £10 10s. secures (in addition to the use of the Laboratory) permission to attend the Lectures in Physics and Mathematics as well as Chemistry, and to use the Physical Laboratory and Engineering Workshop.

The College Day Classes re-open on Sept. 17, and the Evening Classes commence on Monday, September 30.

Further detailed information may be obtained from the College Calendar, price 6d., or the Prospectus for Day or Evening Classes (free).

UNIVERSITY OF BIRMINGHAM.

Professor—Percy F. Frankland, Ph.D., M.Sc., LL.D F.R.S., P.I.C.
Assistant Lecturers and Demonstrators—Alex. Findlay, M.A., D.Sc., Ph.D.; Hamilton McCombie, M.A, Ph.D., B.Sc., A.R.C.S., A.I.C.; C. K. Tinkler, B.Sc., and T. J. Murray, Ph.D.

The Session will be opened on October 1st, 1907.

Lecture Courses.

First Year.—A. This part of the course is arranged (1) to give a full exposition of the general principles of Chemical Science, (2) for the systematic study of the properties of the more important elements and their compounds, and (3) to indicate the chief applications of Chemistry in the Arts and Manufactures. Four hours weekly during the Winter and Spring terms. Mondays to Thursdays inclusive, at 9.30 to 10.30 a.m. Fee, £5 5s. B. This part of the course includes an introduction to the study of Organic Chemistry, with a description of the properties, relations, and methods of preparation of the more important groups of Carbon Compounds. Three hours weekly during the Summer term. Mondays, Wednesdays, and Fridays, at 9.30 to 10.30 a.m. Fee, £1 11s. 6d.

Second Year.—Advanced Organic Chemistry.—This course extends over two years, and is divided into two parts:—(*a*) Carbon Compounds of the Fatty Series; (*b*) Aromatic and other Cyclic Compounds. Only one of these parts will be taken in each year. The class meets twice weekly by arrangement during the Winter and Spring terms. Fee, £2 2s. *General and Physical Chemistry.*—This course will deal in outline with the more recent developments of Theoretical Chemistry. The class meets once weekly by arrangement during the three terms. Fee, £1 11s. 6d.

Third Year.—A further Course in Advanced Organic Chemistry will deal with one of the above parts of the Course. The class meets two hours weekly by arrangement during the Winter and Spring terms. Fee, £2 2s. A further Course on General and Physical Chemistry, in which special subjects attracting attention at the time receive treatment. Fee, £1 11s. 6d.

Practical Chemistry.

The instruction in Practical Chemistry extends over three years. The Laboratory will be open daily from 9.30 to 5, except Saturdays, when it closes at 1 p.m. Fees—

	All day.	Three hours per day.	Three hours per day; five days a week.	Three hours per day; three days a week.
	Guineas.	Guineas.	Guineas.	Guineas.
One Term ..	7	4½	4	2½
Two Terms .	13	8½	7½	5
Three Terms	18	12	11	6½

A Course of short demonstrations and exercises is given by the Professor or one of his Assistants once a week. All first-year Students are required to attend, unless exempted for special reasons by the Professor. No Fee.

Special facilities are given to Advanced Students for the prosecution of original research.

Metallurgy.

There is a separate University department for Metallurgical students in which provision is made for instruction in assaying, &c.

Scholarships.

Priestley Scholarships.—Three Open Scholarships in Chemistry of the value of about £96 each are awarded annually in June.

Ascough Scholarship.—One Open Scholarship of the value of about £30 is awarded annually in July.

Bowen Scholarship.—One Open Scholarship in Metallurgy, value about £96, is awarded annually in June.

For particulars apply to the Registrar.

Excursions.

During previous Sessions permission has been obtained to visit some of the great factories in or near Birmingham, in which chemical and metallurgical industries are carried on. Students have thus had most valuable opportunities of gaining a practical acquaintance with some branches of Applied Science. The privilege thus courteously granted by several manufacturers will, it is hoped, be enjoyed in every future Session. The excursions will be conducted by the Professor or Lecturers.

CITY OF BRADFORD TECHNICAL COLLEGE.

Principal—Prof. W. M. GARDNER, M.Sc.

DEPARTMENT OF CHEMISTRY AND DYEING.

Professor of Chemistry and Dyeing—W. M. Gardner, M.Sc.
Assistant Professor of Chemistry—B. North, A.R.C.Sc. (Lond).
Lecturers in Chemistry—L. L. Lloyd, Ph.D.; S. F. Stell, F.C.S.
Demonstrators in Chemistry—S. M. Sutcliffe, F.C.S.; S. R. Illingworth.
Lecturer in Physics—J. A. Tomkins, A.R.C.Sc. (Lond.).
Demonstrator in Physics—E. B. Walker.
Lecturers in Dyeing—A. Herz, Ph.D., and A. B. Knaggs F.C.S.
Demonstrator in Dyeing—L. Minikin.
Lecturer in Gas Manufacture—W. Cranfield.
Lecturer in Botany, Biology, and Pharmacy—W. West, F.L.S., Ex. Pres. Yorkshire Naturalists' Union.

The following courses of instruction are provided:—

I. *General Chemistry Course*, extending over four years, including Lectures in Inorganic, Organic, and Technological Chemistry, Principles of Analysis, Technical Analysis, Electro-chemistry, Physical Chemistry, Crystallography, Fuels, Lighting and Ventilation, Physics, Mathematics, Mechanics, with Laboratory work in Chemistry, Physics, Bacteriology, and Microscopy.

II. *Chemistry and Dyeing*, extending over four years. Includes most of the above subjects, along with Lectures and practical work in Dyeing, Colour matching, &c.

III. *Chemical Engineering*. Three years' course, preparing Students for positions in Chemical Works, Sewage Works, &c.

IV. *Sanitary Science*. One year's Course, recognised by the Sanitary Institute as preparing for their certificate examination. Subjects: Chemistry, Physics, Sanitary Engineering, Sanitary Law, Building Construction, Drawing, Physiology, and Bacteriology.

V. *Dyeing*. Extending over one or two years.

VI. *Textile and Dyeing*. Arranged for those Students who desire to study the two subjects simultaneously.

VII. *First Professional Examination, Conjoint Medical Board (M.R.C.S., L.R.C.P.), London*.—Attendance at the College and College Certificates in Chemistry, Physics, and Biology are recognised by the Conjoint Board for Medical Studies as a qualifying curriculum.

VIII. *General Pharmaceutical Course*. Prepares for the Minor and Major Pharmaceutical Examinations. Each extends over two years on four half-days per week, and includes Chemistry and Physics, Botany, Biology, Materia Medica, Pharmacy, and Dispensing.

ROYAL AGRICULTURAL COLLEGE, CIRENCESTER.

Chemical Department.

Professor—Prof. E. Kinch, F.C.S., F.I.C.

Assistant—W. James.

Systematic courses of Lectures are given on the various branches of Chemistry in its relation to Agriculture, illustrated by experiments, and by the collections in the College Museum. They comprise the laws of Chemical Combination and the general Chemistry of mineral bodies, and of the more frequently occurring bodies of organic origin, with the relationships of their leading groups; and, finally, the applications to practical operations of the Chemistry of the atmosphere, of soils and manures, of vegetation, of stock feeding, and of the processes and products of the dairy.

In the Laboratory practical instruction is given in the construction and use of apparatus and in Chemical manipulation and analysis, both qualitative and quantitative. After studying the simple operations and the properties of the commonly occurring substances, the Students are taught to analyse a series of compounds, and apply the knowledge thus obtained to the analysis of manures, soils, waters, feeding stuffs, dairy products, and other substances met with in the ordinary course of Agricultural practice. Chemico-agricultural researches are undertaken by the senior Students under the direction of the Professor and his Assistants.

THE UNIVERSITY OF LEEDS.

Professor of Chemistry—Arthur Smithells, B.Sc., F.R.S.

Professor of Organic Chemistry—Julius B. Cohen, Ph.D., B.Sc.

Lecturer on Physical Chemistry—H. M. Dawson, D.Sc., Ph.D.

Assistant Lecturer and Demonstrator—W. Lowson, B.Sc., F.I.C.

Demonstrators—W. H. Perkins, B.Sc.; H. Calam, M.Sc.; A. T. King, B.Sc; J. Marshall, B.Sc.

The Session begins October 1, 1907.

Lecture Courses.

1. General Course of Chemistry.—Monday, Wednesday, and Friday, at 11.30 a.m. Fee for the Course, £4 4s.

2. Advanced Inorganic Chemistry.—Metals. Monday, Wednesday, and Friday, at 9.30 a.m. Fee, £3 13s. 6d.

3. Advanced Inorganic Chemistry.—Non-metals. Tuesday, Thursday, and Saturday, at 9.30 a.m. Fee, £3 13s. 6d.

4. Organic Chemistry. — Tuesday, Thursday, and Saturday at 12 noon Fee £3 13s. 6d.

5. Honours Courses.—(*a*) Organic Chemistry: Monday, Wednesday, and Friday at 12 noon in the First and Second Terms; fee, £2 12s. 6d. (*b*) History of Chemistry: Monday, Wednesday, and Friday at 9.30 a.m. in the First Term; fee, £1 11s. 6d. (*c*) Physical Chemistry: Monday, Wednesday, and Friday at 9.30 a.m. in the Second and Third Terms; fee, £2 12s. 6d. (*d*) Electro-chemistry: One hour weekly; 31s. 6d.

6. Chemistry of Food and Drugs.—Special class for Students taking Final Examination of the Institute of Chemistry in Branch E (Food and Drugs). £2 2s.

Laboratory Courses.

The University Laboratory will be open daily from 9 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it will close at 1 p.m.

Fees for the Session.—Students working six days per week, £21; five, £18 18s.; four, £16 16s.; three, £13 13s.

Practical Course in Sanitary Chemistry.—Tuesdays and Thursdays from 2 to 5 from April to June. Fee, £5 5s.

Dyeing and Tinctorial Chemistry Department.

Professor—Arthur G. Green, M.Sc., F.I.C.

Lecturer and Research Chemist—A. G. Perkin, F.R.S., F.I.C.

Assistant Lecturer—A. B. Steven, B.Sc.

Demonstrator—Ian Q. Orchardson, B.Sc.

The Courses extend over periods of three or four years, and are intended for those who wish to obtain a full scientific and practical education in the art of dyeing, &c. It is suitable for those who purpose in the future to take any part in the direction of the operations of dyeing or printing of textile fabrics, *e.g.*, the sons of manufacturers, calico printers, managers, master dyers, &c.

Leather Industries Department.

Professor—H. R. Procter, M.Sc., F.I.C.

Assistant Lecturer and Demonstrator—F. Kopecky.

Demonstrator—Harold Brumwell.

Research Assistant—H. G. Bennett, M.Sc.

The full Courses, which extend over a period of either two or three years, are suitable to all who intend to become Technical Chemists in the Leather Industry, or managers of important works, and are recommended to sons of tanners. The Courses include instruction in chemistry, a modern language, leather manufacture, and practical work in the Leather Industries Laboratory and Dye-house.

Agricultural Department.

Professor—R. S. Seton, B.Sc.

Lecturer in Agricultural Chemistry—C. Crowther, M.A., Ph.D.

The full Course occupies two years, and includes instruction in chemistry, physics, mathematics, geology, botany, forestry, engineering and surveying, and the principles of agriculture, as well as practical work in the various laboratories and out-door agriculture.

Fuel and Metallurgical Department.

Professor—William A. Bone, D.Sc., Ph.D, F.R.S.

The Courses extend over two, three, or four years, and are suitable for those who are preparing for posts either as Gas Engineers or in Fuel and Metallurgical industries.

The Courses in Gas Engineering and the Technology of Fuel will chiefly deal with the manufacture and distribution of coal-gas and gas-lighting problems, by product coking processes, and the production and application of gaseous fuels for heating and power purposes.

The Metallurgical Courses, besides dealing with general processes for the concentration and extraction of ores, will be chiefly directed to problems underlying blast furnace and open-hearth steel practice, and to the microstructure, physical properties, and heat treatment of steel and other industrial alloys.

Research Students are admitted to the University Laboratories on reduced terms.

Several valuable Fellowships and Scholarships are at the disposal of the University, including a Fellowship of £100 offered by the Institution of Gas Engineers, and the Salt, Akroyd, Brown, Baines, Emsley, Craven, Leeds City Council, and Clothworkers' Scholarships, and one of the 1851 Exhibition Scholarships. The North, East, and West Ridings County Council's Scholarships are tenable at the University of Leeds.

UNIVERSITY OF LIVERPOOL.

Professor of Chemistry—J. Campbell Brown, D.Sc.

Professor of Physical Chemistry—F. G. Donnan, M.A. Ph.D.

Lecturer on Organic Chemistry—A. W. Titherley, D.Sc., Ph.D.

Lecturer on Metallurgy — Guy D. Ricketts, M.A., A.R.S.M.

Demonstrators and Assistant Lecturers — A. T. de Mouilpied, M.Sc., Ph.D.; H. Bassett, B.Sc., Ph.D., D.es.Sc.; F. J. Brislee, D.Sc.; A. Rule, M.Sc., Ph.D.; E. Garratt, M.Sc.; and T. E. Gardner, B.A., B.Sc.

Assistant—H. H. Froysell.

The Session commences October 8th.

Entrance Scholarship Examination takes place early in May each year.

The Classes meet the requirements of candidates for the Ordinary B.Sc. Degree, for Chemistry Honours, or for the M.Sc. or D.Sc. Degree in the University of Liverpool; for Degrees in Medicine of Liverpool; for the Pharmaceutical, Veterinary, Dental, and Public Health Diplomas; and for those studying Chemistry as a preparation for professional, technical, or commercial life. The Classes qualify for the Fellowship of the Institute of Chemistry and other Examination Boards.

Lecture Courses.

A. General Course on the principal non-metallic elements and the most important metals, the principles of Chemical Philosophy, and an introductory sketch of Organic Chemistry. Three Terms. Fee, £4.

Engineer's Course of Lectures with Practical Class. Two Terms. Fee, including Practical class, £3.

Pharmacy Courses: Junior, £3; Senior, £3.

Course B.—Inorganic Chemistry. Fee, £3.

Course C.—Inorganic Chemistry (Honours Course). Fee, £2 10s.

Course D.—Organic Chemistry. Fee, £3.

Course E.—Organic (Honours). Fee, £4.

Course F.—Physical Chemistry. Fee, £3.

Course G.—Honours Physical Chemistry. Fee, £4.

Course H.—History of Chemistry and Chemical Philosophy. Fee, £2.

Courses J. — Applied Chemistry and Metallurgy: Lectures on Technology are given in connection with Laboratory work at hours to be arranged. The subjects are varied in different years. (1) Alkali and Allied Manufactures. (2) General Principles of Metullurgy. (3) Iron, Steel, and Aluminium. (4) Copper, Lead, Silver, and Gold, and other Metals. (5) Fuel and Gas. (6) Technical Gas Analysis.

Course K.—Applied Organic Chemistry.

Course L—Applied Electro-chemistry.

Fee (Courses J, K, L), three terms, £2 10s.

Practical Classes.

(1) Junior. (2) Intermediate: Qualitative Analysis; preparation of Inorganic Compounds; simple Quantitative and Volumetric Analysis. (3) Revision Class. (4) Engineers' Class. (5) General Metallurgy (Elementary).

Chemical Laboratory.

The Chemical Laboratories provide accommodation for every kind of chemical and metallurgical work and research. They include thirty rooms devoted to the study of Chemistry and Metallurgy. Separate rooms are provided for Organic Work, Quantitative Analysis, Water and Gas Analysis, Photometry and Photography, Electro-chemical Work, Metallurgy Laboratories, Research Laboratories and Library, and a Museum. Large new Laboratories for Physical Chemistry and Electro-chemistry have been recently erected.

Students desirous of gaining a thorough theoretical and practical acquaintance with Technical Chemistry, or who intend to adopt Chemical work as a profession, must devote three or four years to special study, for which a full curriculum is provided. Fees:—

Per Week.	One Term, Three Months.	Three Terms One Session.
One day	£4	£7
Two days	5 10s.	10
Three days	7	13
Whole week	10 10s.	21

Pharmaceutical Course (see special syllabus).

D.P.H. Course (see special syllabus).

Course for Dental Degree (see special syllabus).

Veterinary Course (see special syllabus).

Technological Curriculum.

The curriculum extends over three or four years.

The Final Examination for the Associateship of the Institute of Chemistry may be taken after the third year. Those students who have taken the Ordinary Degree of B.Sc. may pass the M.Sc. Exam. in any subsequent year.

The Sir John Willox Chemical Scholarship of £50 per annum, tenable for two years, will be competed for in December, 1907, on an Examination in subjects which are included in the first two and a half years of the above curriculum. Candidates should send in their names to the College Secretary not later than November 15. The Sheridan Muspratt Scholarship, on similar lines, will be open for competition in December, 1908. Other Scholarships, Entrance Scholarships, and Free Studentships are also available to Students.

Evening Classes.

Classes on Metallurgy and Physical Chemistry will be held during the winter.

Prospectuses containing particulars may be obtained from the Registrar, University of Liverpool.

ARMSTRONG COLLEGE, NEWCASTLE-ON-TYNE.

Professor of Chemistry—P. Phillips Bedson, M.A., D.Sc., F.I.C., F.C.S.

Lecturer in Chemistry—F. C. Garrett, D.Sc., F.C.S.

Assistant Lecturer and Demonstrator—J. A. Smythe, M.Sc., Ph.D.

Demonstrator—A. A. Hall, M.Sc., Ph.D.

Lecturer in Agricultural Chemistry—S. Hoare Collins, M.Sc., F.I.C., F.C.S.

Assistant to Lecturer in Agricultural Chemistry—J. Watson, B Sc.

First Year Courses.—I. *General Course.*—This Course o Lectures will extend over the three terms of the Session, and is intended to serve as an introduction to the Science. The Lectures will be of an elementary character, and whilst framed to meet the requirements of First Year Students will also be serviceable to such as intend pursuing Chemistry in its various applications in the arts and manufactures, as, for instance, Brewing, Metallurgy, the Manufacture of Soda, Soap, Glass, &c. The subjects treated will include an exposition of the Principles of Chemistry, and a description of the preparation and properties of the chief Elementary Substances, both metallic and non-metallic, and their more important native and artificial compounds. The class will meet on Mondays, Wednesdays, and Fridays, at 11 a.m., and will commence on Wednesday, October 9th. Fee, £3 10s. for the Session.

II. *Special Course.*—More advanced than the above. Wednesdays and Fridays, 11 to 12. Fee, £3 10s. for Session.

For Diploma in Electrical Engineering.—Tuesday, 12 to 1. A course of Lectures will be given dealing with the Principles of Chemistry, Fuel, the Phenomena of Combus-

tion, and Metals and Alloys employed in Engineering, &c. Fee for the course, £2.

Second Year Courses.—The Lectures for the second year students consist of a course of Lectures on Organic Chemistry, and a course of Lectures on Inorganic Chemistry. The class on Organic Chemistry will meet on Tuesdays and Thursdays at 11 a.m., and will commence on October 8th. The class for Inorganic Chemistry meets at 11 a.m. on Mondays. Fee for Session, £3 10s.; for Inorganic alone £1 10s.; and for Organic alone £3.

Third Year Courses.—Advanced Classes are held for the study of Inorganic, Organic, and Theoretical Chemistry. Fee for the course, £3 10s.

A Lecture Course in Analytical Chemistry will be given on Fridays, at 9.15 a.m. Fee for the course, £1.

Metallurgy and Assaying.—Lecturer, Professor Louis, M.A., F.I.C., F.C.S.; Demonstrator, H. Dean, A.R.C.M. A Metallurgical Laboratory is provided, in which instruction is given in the ordinary processes of Dry Assaying, and in the preparation and analysis of Alloys, &c. Fees as for Chemical Laboratory.

Agricultural Chemistry.—The instruction in this branch of Chemistry will consist of a series of Lectures and of special practical work in the Chemical Laboratory. Students will be expected to have a knowledge of Elementary Chemistry, such as may be obtained by attending the General Course.

The Lecture Course in Agricultural Chemistry is arranged for two days a week throughout the Session. Fee, £3 10s.

Practical Chemistry.—The Laboratory is open from 10 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it closes at 1 p.m. *Laboratory Fees.*—Students working two days, £3 10s. per term, £9 per session; one day per week, £2 per term, £5 per session.

Courses of Study.—Students will be divided into two classes:—(1) Regular, or Matriculated Students, who are also Members of the University of Durham; and (2) Non-Matriculated Students. Regular Students will be required to follow such a course of study in the subjects professed in the College as will enable them to pass the Examinations for the degree of Bachelor in Science of the University of Durham. Non-Matriculated Students will attend such classes as they may select. Every candidate for admission as a matriculated student must pass an examination on entrance, in the following subjects:—Arithmetic; English Essay; Geometry; the subject-matter of Euclid, Books I., II., III.; Algebra, up to and including Quadratic Equations. Also any two of the following:—English Language; Latin, including Grammar and Easy Sentences; Greek; French; German; Geography. The next examination commences on September 30. Names to be sent in at least ten days before this date. Registered students in medicine are exempted from this examination, or students who produce a certificate of having passed either of the three following examinations:—1. The first examination for the Degree of B.Litt. 2. Durham Examination for certificate of proficiency in General Education, held in March and September. 3. Durham Examination for Students in Arts in their first year, or any examination of a similar nature that may be accepted by the Council.

The University has recently adopted the following Matriculation Examination for students entering the Faculty of Science:—Additional Mathematics; English; English History; any *one* subject selected from Religious Knowledge, Botany, Zoology, Physical and General Geography, Experimental Science; any *two* subjects selected from Latin, Greek, French, German. (Students may substitute Extra Mathematics for one of these optional subjects up to and including September, 1911).

In order to enter on a three years' course of study for a Degree in Letters a student must have previously satisfied the Examiners in the following subjects:—Elementary Mathematics or Additional Mathematics; English; English History; either Latin or Greek; either French or German; *one* of the following subjects—Religious Knowledge, Botany, Zoology, Physical and General Geography. Experimental Science.

For detailed Syllabuses and complete Regulations the College Calendar should be consulted.

Bachelorship in Science.—Every candidate for the Bachelorship in Science will be required to satisfy the examiners in Mathematics, Physics, Chemistry, and either Geology or Natural History—in an examination to be held at the end of the candidate's first year, and at the end of the third year in an examination in one chief and two auxiliary subjects. For details of the subjects the College Calendar should be consulted. Candidates may qualify for the degree of B.Sc. by attending special courses in Agriculture, Engineering, and Mining, and passing the several examinations.

Exhibitions.—Two Exhibitions of the value of £20 and £10 respectively will be awarded in September next to Candidates desirous of attending the first year course of study in the College.

The examination will be held at the College, and will commence on Thursday, October 3rd.

Evening Lectures.—Courses of Evening Lectures will be given, with a Practical Class for Laboratory instruction.

Several valuable Scholarships are available for students, including the Johnston Chemical Scholarship of the value of £60 for one year, which is open to Bachelors of Science of any British University; the examination for this Scholarship will be held during the week commencing September 30th. Candidates should send in their names to the Secretary on or before September 20th.

THE UNIVERSITY OF MANCHESTER.

Professor and Director of the Chemical Laboratories—Harold B. Dixon, M.A., M.Sc, F.R.S.

Professor of Organic Chemistry—W. H. Perkin, Ph.D., F.R.S.

Senior Lecturers and Demonstrators—G. H. Bailey, D.Sc., Ph.D.; C. Weizmann, Ph.D.; Norman Smith, M.Sc.

Assistant Lecturers and Demonstrators—E. C. Edgar, D.Sc.; H. F. Coward, M.Sc; Ida Smedley, D Sc.; and J. L. Simonsen, M.Sc.

Lecturer in Organic Chemistry—J. F. Thorpe, Ph.D.

Professor of Metallurgy—H. C. Carpenter, M.A., Ph.D.

Lecturer in Electro-Chemistry—R. S. Hutton, D.Sc.

The Session begins October 1, 1907.

The Chemical Classes form part of the Courses for Degrees in the University.

Chemistry Lecture Courses.

General Chemistry Course.—Tuesdays, Thursdays, and Saturdays, at 9.30, during the two Winter Terms.

Introduction to Organic Chemistry.—Wednesdays and Fridays, at 9.30, during the Lent Term.

These courses are intended for Students commencing the study of chemistry.

First Year Honours Course.—Mondays, Wednesdays, and Fridays, 11.30, during the two Winter Terms. The Non-Metals.

Second Year Honours Course.—Mondays, Wednesdays, and Fridays, at 2, during the two Winter Terms. The Metals.

Third Year Honours Course.—Theoretical and Physical Chemistry.

Organic Chemistry (General).—Mondays and Fridays, at 9 30, during the two Winter Terms.

Organic Chemistry (Advanced).—Tuesdays and Wednesdays, at 9.30, during the two Winter Terms.

History of Chemistry.—Short Courses during the two Winter Terms.

Metallurgy.—Introductory Course, followed by either—(A) Lead, Copper, Bismuth, Antimony, Zinc, and Tin; or (B) Iron and Steel. Each Course, one Lecture per week during the Session.

Electro-chemistry.—General Theoretical Course: Two hours per week during the Michaelmas Term.

Applied Electro-chemistry: One hour per week during Lent and Easter Terms. A course of six lectures on the Electric Furnace and its Applications will be given on Saturday afternoons during the Michaelmas Term.

Applied Chemistry.—(1). Sulphuric Acid and Alkali Manufactures; General Principles of Chemical Engineering. (2). The Natural and Artificial Colouring Matters and the Principles of Dyeing and Printing. (3). The Chemistry of Fuel.

Chemistry Laboratory Courses.

During the first year, the student works in the "Roscoe" or the "Dalton" Laboratory at Qualitative Analysis and Inorganic Preparations. Second Year Students work at Quantitative Analysis, and also take a Laboratory Course in Physics or some other subject. Third Year Students work in the "Schorlemmer" Laboratory of Organic Chemistry, and may also undertake experimental work in some special branch of Chemistry.

The Chemical Laboratories are open daily from 9.30 a.m. to 4.30 p.m., except on Saturdays, when they are closed at 12.30 p.m.

Metallurgical Laboratory.—This has been recently much enlarged and re-equipped, mainly with a view to post-graduate work on the Structure of Metals and the Chemistry of Fuel.

Applied Organic Chemistry.—In connection with the "Schorlemmer" and "Schunck" Laboratories, a special laboratory is fitted with apparatus and appliances suitable for investigations on Dyes and other organic substances on a large scale.

Electro-chemical Laboratory.—In addition to such apparatus as is required for experimental work on Electrolysis and the Electro-deposition of Metals, special equipment is provided for investigations with the Electric Furnace.

Chemical Research.

In addition to the facilities mentioned above for Metallurgical and Electro-chemical Research, the following laboratories are available for post-graduate work:—(1) The private Laboratories of the two Professors; (2) The "Frankland" Laboratories for Physical Chemistry; (3) The "Schunck" Laboratory for Organic Chemistry; (4) The "Thorpe" Laboratory for Organic Chemistry.

To encourage post-graduate work of this kind, the University gives a "Beyer" Fellowship (£100 per annum) and Scholarships (£50 per annum).

The "Dalton" Chemical Scholarship (£50 per annum, tenable for two years) is also awarded, and the 1851 Exhibition Scholarships (£150) may be held in the Laboratory. Further, Honorary Research Fellowships and Research Studentships are granted from time to time to those who are capable of carrying out original investigations.

Two "Schunck" Research Assistants are appointed annually.

Courses for Degrees.

To qualify for the Ordinary Degree of B.Sc. Students have to attend a prescribed course of study extending over three years, and are recommended to pass the Matriculation Examination before entrance. (Subsequent to October, 1906, three years attendance *after* matriculation will be compulsory).

The course of the Degree of B.Sc. with Honours in Chemistry is as follows:—First year: First year Honours Lectures; Mathematics (3 hours a week); Physics (3 hours a week); an additional course (3 hours a week); Chemical Laboratory (3 days per week). Second year: Second year Honours Lectures; General Organic Lectures; Physical or some other Laboratory (1 day per week); Chemical Laboratory (3 days per week). Third year: Third year Honours Lectures; Lecture course in some Special Branch of Chemistry; History of Chemistry; Chemical Laboratory (5 days per week, for one of which attendance in another Laboratory may be substituted).

For the M.Sc. Degree post-graduate work is required. The D.Sc. may be obtained after four years from graduation, provided that the candidate has distinguished himself in research.

Certificate in Applied Chemistry.—The course extends over three years, and comprises systematic instruction by means of lectures and practical work in the laboratories.

For further particulars of any of these courses apply to the Registrar, Edward Fiddes, M.A.

UNIVERSITY COLLEGE, NOTTINGHAM.

DEPARTMENTS OF CHEMISTRY AND METALLURGY.

Professor of Chemistry—F. Stanley Kipping, Ph.D., D.Sc., F.I.C., F.R.S.

Demonstrators of Chemistry—R. M. Caven, D.Sc., F.I.C.; G. Sand, D.Sc.; and G. Martin, Ph.D, B.Sc.

The Classes of the College are open to students of both sexes above sixteen years of age.

The Session commences October 7th, for both Day and Evening Classes.

Lecture Courses.—The Chemistry Day Lectures extend over three years. In the first year a student enters for the course on Elementary Chemistry. In his second year he attends Lectures on both Inorganic and Organic Chemistry. In his third year he attends courses on Advanced Organic Chemistry, Physical Chemistry, and Advanced Inorganic Chemistry.

The fees for the Day Lectures and Classes are as follows: First year, two Lectures per week, 15s. per term. Second year, three Lectures per week, 22s. 6d. per term. Third year, four Lectures per week, 30s. per term.

Demonstrations and Lectures on Analytical Chemistry are given, and Chemical Calculation and Tutorial classes are also held. Various short courses of lectures on special subjects are delivered during the Session.

Students may qualify themselves by attendance at these lectures and classes for the Examinations of the Universities of London, Cambridge, or Oxford, and for the Medical Examinations of the Royal College of Surgeons and of the Universities of Cambridge and Edinburgh: they may also obtain instruction in Chemistry for technical or other purposes, and can enter for a full Chemical Engineering Curriculum. Special attention is given to the requirements of candidates for the Associateship of the Institute of Chemistry.

Practical Chemistry and Metallurgy.—The Chemical and Metallurgical laboratories are open every day from 9 to 5, except on Saturday, when the hours are from 9 to 1; also on Tuesday and Thursday evenings from 7 to 9. Each Student works independently of other Students at a course recommended by the Professor. Instruction is given in general Chemical Manipulation, in Qualitative and Quantitative Analysis, and in the methods of Original Chemical Investigation and Research; Students are also enabled to work out the applications of Chemistry to Pharmacy, Metallurgy, Dyeing, Agriculture, Brewing, Iron and Steel, Tanning, and other Manufacturing Processes. Fees for day students: For one term, £7; for the session, £18; for six hours weekly 40s., and 5s. extra for each additional hour per week. Evening students, 10s. for 2 hours per week, 3 hours 15s., 4 hours 20s., per term.

Research Work.—Students or others wishing to undertake research work in pure or Applied Chemistry will be afforded every facility for doing so and may be admitted at reduced fees. The Laboratories are fully equipped with apparatus and chemicals necessary for such work.

Courses of Technical Chemistry Lectures are also given on Engineering, Dyeing and Bleaching, Brewing, Plumbing, Bread-making, Gas Manufacture, and on other processes of applied Chemistry.

Pharmaceutical Students are provided with Lectures and Laboratory work suitable for the preparation for the Minor and Major Examinations.

Evening Classes.—Evening Lectures and Laboratory instruction will be given in Pure and Applied Chemistry, and the laboratories are open for practical work on Tuesday and Thursday evenings from 7 to 9. Fee for each Lecture Course, 5s.; for each Laboratory Course, 10s.

Full information concerning all College Classes is given in the College Prospectus, price one penny.

THE UNIVERSITY OF SHEFFIELD.

Professor of Chemistry—W. P. Wynne, D.Sc., F.R.S.

Lecturers and Demonstrators—W. E. S. Turner, M.Sc., B.Sc.; W. J. Jarrard, B.Sc.; C. R. Young, B.Sc.

The Session will commence October 2nd.

Matriculation Course. — Tuesday and Friday at 9 30. Fee, £2 12s. 6d., and three hours per week Laboratory work.

Candidates for the Intermediate Examination are required to satisfy the Examiners in three of the following subjects:—Pure Mathematics, Applied Mathematics, Physics, Chemistry, and Biology. And those for the Final Examination in three of the following subjects:—Pure Mathematics, Applied Mathematics, Physics, Chemistry, Zoology, Botany, Physiology, Geology, Education.

Intermediate Course in Chemistry for B.Sc. or M.B.—Monday, Tuesday, Thursday, and Friday at 9 30 a.m. £5 5s., and nine hours per week Laboratory work.

B Sc. Course in Chemistry.—Tuesday and Wednesday at 5 p.m., with another hour to be arranged, £4 4s., and 12 hours per week Laboratory work during two Sessions.

B.Sc. with Honours.—Honours Students in Chemistry, after passing the Intermediate Examination, devote the whole of their time to the study of Chemistry, and are expected to reach the standard for a pass in Chemistry for the ordinary degree by the end of the second year. During the second or third year they devote one day a week to lectures and practical work in a subsidiary subject—Mathematics, Physics, or Metallurgy—selected for the degree. The third year is devoted to the advanced study of Chemistry, either chiefly Physical and Inorganic or chiefly Organic, as the student may select. At least four days a week during the second and third years are spent in the laboratory.

M.Sc.—This degree may be conferred upon a Bachelor of Science with Honours who is of one year's standing from the date of his graduation as a Bachelor of Science, or upon any Bachelor of Science who has either passed an examination in an Honours School subsequent to graduation, or has for at least one year after graduation done research work at the University, and has presented a thesis, approved by the Faculty of Pure Science, upon the research work done during that period.

D.Sc.—The degree of Doctor of Science may be conferred upon any Master of Science of not less than five year's standing from the date of his admission to the degree of Bachelor, provided that he has published, in recognised journals or transactions, a research or researches of special merit and approved by the Faculty of Pure Science as qualifying him for the degree.

Laboratory.—Working hours to be arranged between Professor and Students.

Sessional Fees for Day Students:—Three hours per week, £3 3s.; Six, £5 5s.; Nine, £7 7s.; Twelve, £9 9s.; Eighteen, £12 12s.; Twenty-four, £14 14s.; Thirty-two, £16 16s.; Honour or University Students taking eighteen hours or more per week, £12 12s.

Students joining the Laboratory at Christmas will be charged two-thirds and at Easter one-third of the Fees for the whole Session.

A Course of Lectures, with a special class in Laboratory Work, is arranged for Medical Students entering for the Conjoint Board Examinations. Fee, £7 7s.

A course of Elementary Practical Physics and Practical Chemistry, which will meet the requirements of candidates for the Diploma of Public Health will be held during the Michaelmas and Lent terms. Fee £5 5s.

An arrangement has been entered into with the Board of Education, South Kensington, which will enable Science Teachers to work in the Chemical Laboratory for three, six, or twelve hours a week on payment of one-quarter of the usual fee, the Board being willing to pay the remainder under certain conditions, of which full information may be obtained on application to the Registrar.

Evening Classes.—Lecture Class and Laboratory, on Wednesday evening during the Michaelmas and Lent terms. Fee, £1 10s.

Department of Metallurgy.

Professor of Metallurgy—J. O. Arnold. This Department has been equipped to meet the requirements of the local industries. The Laboratory is fitted with the most modern apparatus for metallurgical analysis, more especially with appliances for the rapid and accurate chemical examination of Iron and Steel, Fuel, and Refractory materials. It also contains a complete pyrometric installation, and a laboratory for the study of the micrographic analysis of metals fully equipped with specially designed microscopes by Ross, polishing tables, etching appliances, incandescent light for evening work, &c. The School is now the most complete of its kind for teaching the practical manufacture, the chemical constitution, and the physical properties of Steel. Special attention is given to the determination of the microscopic constituents of Steel. Although the chief industry of the district occupies the central position in the course of instruction, general metallurgy is not neglected, but is dealt with in a separate syllabus, dealing with metals (other than iron and steel) used in the arts. Students are thus enabled to select and at once enter upon a course of scientific metallurgical training of immediate practical utility. They may take up and work through any portions of the course, but certificates will be granted only to those who follow the prescribed courses, and pass the necessary examinations. Lectures on Iron and Steel Manufacture, on Fuel and Refractory Materials, and on General Metallurgy. Practical Metallurgy:—Laboratory, Furnaces, Foundry, and Testing Machine Course; Practical Course of Metallurgy other than Iron and Steel; Practical Fuel Course for Students in Collieries or Gas Works.

A new steel works has recently been erected in connection with the Sheffield College at a cost of about £10,000. The works include a two ton open-hearth furnace, a one ton Bessemer plant, and a four-hole crucible melting plant. The works is also provided with a hammer capable of dealing with four-inch ingots Differential annealing furnaces, oil brightening and lead-tempering tanks will constitute part of the new plant. Additional laboratory accommodation is attached to the works, viz., chemical laboratory for staff, chemical laboratory for post graduate students, together with a complete magnetic laboratory for hysteresis, &c.

UNIVERSITY COLLEGE, DUNDEE.

University of St. Andrews.

Professor of Chemistry—James Walker, Ph.D., D.Sc., F.R.S.

Assistant Lecturers—J. S. Lumsden, Ph.D., D.Sc., and J. K. Wood, D.Sc.

Lecture Assistant and Lab. Steward—J. Foggie, F.C.S.

The Winter Session begins early in October and ends in March. The Summer Session extends from the middle of April to the end of June.

The Junior Lecture Course on Systematic Chemistry is given daily during the Winter Session, and embraces the Elements of Inorganic and of Organic Chemistry.

Advanced Courses, of about fifty lectures each, will be given during the year as follows:—

Organic Chemistry; Inorganic Chemistry, including the more important technological applications; Theoretical and Physical Chemistry; Bleaching and Dyeing, including the Chemistry of the Textile Fibres.

Practical Instruction in all of the above branches will be given in the Laboratories and Dye-house. Special facilities are afforded to Research Students.

UNIVERSITY OF ABERDEEN.

Chemistry.

Professor—Francis R. Japp, M.A., LL.D., F.R.S.

Demonstrators—Francis W. Gray, M.A., B.Sc., and Joseph Knox, D.Sc.

I. *General Lecture Course* (100 *Lectures*).—Daily during the Winter Session. The subjects treated of include (1) The Laws of Chemical Combination and the General Principles of Chemistry; (2) Non-metallic and Metallic

Elements, and their Compounds; (3) Organic Chemistry; (4) Applications of Chemistry to the Arts and Manufactures. Fees, for first attendance, £4 4s.; for subsequent attendance, £3 3s. A Tutorial Class (without fee), conducted by the Junior Demonstrator, is held in connection with this course.

II. *Special Lecture Course on Organic Chemistry* (50 *Lectures*).—Daily during the Summer Session. Fee, £3 3s.

III. *Practical Course for Medical Students.*—This course, which occupies five hours a week during the Summer Session—in all fifty hours—is devoted to practice in Elementary Qualitative Analysis. Fee, £3 3s.

IV. *Chemical Laboratory.*—The Laboratory is open to Students daily from 9 a.m. to 5 p.m. Each Student on entering is allowed to arrange his hours of work so as to suit his own convenience, but must adhere to these hours when once fixed. The Laboratory instruction includes: (1) General experiments; (2) Preparations; (3) Qualitative analysis; (4) Quantitative analysis: gravimetric, volumetric, and gasometric. Fee, £3 3s. a session. A certain number of free places are available, on the recommendation of the Professor, and subject to the approval of the Senatus, for research students.

V. *Physical and Advanced Inorganic Chemistry* (30 *Lectures.*—In connection with the Laboratory work, three Lectures a week on Physical Chemistry and selected portions of Advanced Inorganic Chemistry are delivered during the Winter Session by the Lecturer, Mr. F. W. Gray. Fee, £2 2s.

University of Aberdeen and Aberdeen and North of Scotland College of Agriculture.

Agricultural Chemistry.

Lecturer—James Hendrick, B.Sc., F.I.C.

Assistants—R. Glegg, B.Sc., F.I.C.; W. J. Profeit, M.A., B.Sc.; and H. M. Will, M.A., B.Sc.

I. Preparatory Courses in General Chemistry and in Organic Chemistry are given for those who are unable to take the full University Courses in these subjects. The course in General Chemistry consists of about sixty Lectures with Practical Work (one hour daily) during the Winter Session. The course deals with the general principles of Chemistry, and with those parts of Inorganic Chemistry which are of more immediate concern to students of Agricultural Chemistry. The Practical Work goes along with and illustrates the Lectures. Fee, £4 4s.

The course in Organic Chemistry consists of about thirty Lectures, and is given during the Winter Session. It deals especially with those parts of the subject which are directly related to Agricultural Chemistry. Fee, £1 1s.

II. *Agricultural Chemistry* (*General Course*).—This class meets daily during the Winter Session, and includes both Lectures and Laboratory Work. The Lectures deal with the Chemistry of the Atmosphere, the Soil, Manures, Foods, Preservatives, Insecticides, &c. The Physiological Chemistry of Plants and Animals, the Composition and Manurial Requirements of Crops, and Dairy Chemistry are also treated of. The Laboratory Work is primarily intended to accompany and illustrate the Lectures, Exercises dealing with the properties and composition of Soils, Manures, Feeding-stuffs and Waters, and with the impurities and adulterations of these, occupy much of the time given to Practical Work. The fee for the whole Course (Lectures and Practical Work) is £4 4s.

III. *Laboratory.*—A Summer Course in Practical Chemistry is given to prepare students who have not previously done sufficient laboratory work for the course in Agricultural Chemistry. Fee, £2 2s.

IV. The Laboratory is open daily from 9 a.m. to 5 p.m. for students who wish to study the principles and practice of Agricultural Chemistry or to undertake research in this subject.

UNIVERSITY OF EDINBURGH.

Department of Chemistry.

Professor—Alex. Crum Brown, M.D., D.Sc., F.R.S.

Lecturers—L. Dobbin, Ph.D.; H. Marshall, D.Sc.; and W. W. Taylor, M.A., D.Sc.

The working terms are—Winter Session, from middle of October to middle of March; Summer Session, from beginning of May to middle of July.

Lecture Courses.—During the Winter Session a General Course of Chemistry for medical and science students is given by the Professor. The class meets daily; fee £4 4s. Advanced Courses of 25 lectures each are given in the Winter and Summer Sessions; fee, £1 1s. An Intermediate Course of Organic and Advanced Inorganic Chemistry is held in summer; fee, £2 2s. There is also a class on History of Chemistry or Chemical Theory, by Dr. Dobbin; fee £1 1s.: and a class on Mineralogy and Crystallography, by Dr. Marshall; fee, £2 2s. All these Lectures, except the General Course, are now open to women.

In addition to the above, Lecture Courses are from time to time given by the Assistants on particular branches of Organic and Inorganic Chemistry. These Lectures are free to Laboratory Students.

Laboratories.—Practical classes for Medical Students meet during the Winter Session and in the Summer Session. (Fee, £3 3s.) The laboratories for Science and Arts Students engaged in analytical and advanced practical work are open daily from 9.30 till 4.30. (Fees: Whole Day—Winter Session, £10 10s.; Oct.-Dec., Jan.-March, or Summer Session, £5 5s. Half Day—Winter Session, £6 6s.; Oct.-Dec., Jan.-March, or Summer Session, £3 3s. Preference will be given to students in the above order). Full Courses of instruction are given in Analytical, Practical Organic and Inorganic Chemistry (including Gas Analysis), Physico-chemical Measurements, Agricultural Chemistry, and Assaying. Facilities are afforded to advanced students who desire to undertake chemical investigations.

Various prizes and scholarships are attached to the laboratory and general class.

Graduation.—Two Degrees in Pure Science are conferred, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.).

Candidates for Degrees in Science, if not graduates (by examination) in Arts in one of the Universities of the United Kingdom or in a Colonial or Foreign University recognised for the purpose by the University Court, must pass a preliminary examination in (1) English; (2) Latin, Greek, French, or German; (3) Mathematics; (4) One of the languages Latin, Greek, French, German, Italian, not already taken under (2), or Dynamics. In the case of a student whose native language is other than European, the Senatus may, at the Preliminary Examination, accept such language as a substitute for a modern European language. The Senatus may also in such a case accept as an alternative to Latin or Greek any other classical language, such as Sanscrit or Arabic.

The First B.Sc. Examination embraces Mathematics, or Biology (*i.e.*, Zoology and Botany), Natural Philosophy, and Chemistry. The Final B.Sc. Examination in Pure Science includes any three or more of the following subjects:—Mathematics, Natural Philosophy, Astronomy, Chemistry, Human Anatomy (including Anthropology), Physiology, Geology (including Mineralogy), Zoology (including Comparative Anatomy), and Botany (including Vegetable Physiology). In the Final Examination two written papers are set in each subject professed, the second of a higher standard than the first. Candidates must pass the first section in all, and the second section in at least one, of the subjects professed; the same regulations apply also to the Practical and Oral Examinations. Chemistry in this examination embraces Inorganic, including Mineralogical Chemistry; Organic Chemistry; Physical Chemistry; Chemical Crystallography; History of Chemistry. In the written papers a choice of questions is allowed, so as to adapt the examination to the various courses of advanced study which candidates may have selected. Practical Examination:—Complex Qualitative Analysis; Inorganic Preparations; Gravimetric and Volumetric Analysis. Each candidate taking the higher standard will also be examined on Organic Preparations, Ultimate Organic Analysis, and one of the following subjects, selected by

himself:—Gas Analysis; Assaying; Physico-chemical Measurements, including Practical Crystallography as a special branch.

A candidate for the D.Sc. Degree must submit a thesis on original work done by him. The Thesis must be approved before the candidate is allowed to proceed to Examination. The candidate in Chemistry *may be* required to pass a searching examination in one of the following branches:—(1) The Chemistry and Chemical Technology of Inorganic Bodies, including Metallurgy; (2) Organic Chemistry; and to show a thorough practical acquaintance with chemical analysis in all its branches, and with the preparation of pure substances.

HERIOT-WATT COLLEGE, EDINBURGH.

Principal—A. P. Laurie, M.A., D.Sc., F.R.S.E.
Professor—John Gibson, Ph.D., F.R.S.E.

Assisted by the following Lecturers and Demonstrators:—R. B. Denison, D.Sc., Ph.D.; Archibald Boon, B.A., B.Sc.; Andrew F. King, F.I.C.; E. B. R. Prideaux, M.A., D.Sc.

The Session begins October 1st, 1907.

The curriculum of this College comprises both Day and Evening Classes, each department providing the higher general and technical education.

The Chemistry Course is designed to meet the wants of Manufacturing Chemists. The instruction consists of Courses in Chemistry, Physics, Mathematics, Engineering, and Mechanical Drawing, with Special Courses in Gas and Paper Manufacture, Brewing, &c., by Experts, in the fourth year. Special attention will be paid to Electrochemistry. The Chemistry Classes are recognised by the University as qualifying for the B.Sc., in Chemistry, and are also recognised by the Institute of Chemistry.

For Students who have been three and four years in the Chemistry Department, arrangements have been made for their spending from four to twelve months in the laboratories of the Corporation's Gas Works, with a view to the study of problems connected with the Combustion of Fuel, the Manufacture of Coal-gas and its By-products, &c.

A Laboratory, under the charge of Dr. Emil Westergaard, has been provided for the study of Technical Mycology, including Brewing, Distilling, Malting, Vinegar Making, Tanning, Preserving, Starch and Sugar Making, Bread Making, Butter and Cheese Manufacture, &c.

Matriculation Fee, 5s.; Composition Fees from £12 12s. to £15 15s. Full particulars are published in the Calendar of the College, which is issued early in September.

GLASGOW AND WEST OF SCOTLAND TECHNICAL COLLEGE.

Professor of Chemistry—G. G. Henderson, D.Sc., M.A.
Professor of Technical Chemistry—T. Gray, D.Sc., Ph.D
Professor of Metallurgy—A. Humboldt Sexton, F.C.S., F.R.S.E.

Also, Professors and Lecturers in the other leading branches of Pure and Applied Science and Technology.

Session opens Sept. 23. Entrance Examination Sept. 16.

The main objects of this College are to afford a suitable education to those who wish to qualify themselves for following an industrial profession or trade, and to train teachers for technical schools. It was founded by an Order in Council, dated 26th November, 1886, according to a scheme framed by the Commissioners appointed under the provisions of the Educational Endowments (Scotland) Act, whereby Anderson's College, the Young Chair of Technical Chemistry in connection with Anderson's College, the College of Science and Arts, Allan Glen's Institution, and the Atkinson Institution were placed under the management of one governing body.

The Diploma of the College is awarded to Day Students who have attended prescribed courses of instruction and passed the necessary examinations. The ordinary courses extend over three years, but arrangements are made for advanced students continuing their studies in special departments. The diploma course in Chemistry extends over four years.

Complete courses of instruction are provided in both Day and Evening Classes.

Copies of the Calendar for 1907-1908 may be had from Mr. H. F. Stockdale, Secretary; price by post, 1s. 4d. Prospectuses will be sent free.

UNIVERSITY OF ST. ANDREWS.

UNITED COLLEGE OF ST. LEONARD AND ST. SALVATOR.

Professor of Chemistry — T. Purdie, B.Sc., Ph.D., LL.D., F.R.S.

The Session begins on October 11th. A Competitive Examination, open to intending Students of Arts, Science, and Medicine, for about forty Bursaries, ranging in value from £40 to £10 each per annum, will be held on September 28th and following days. Twenty-four of these Bursaries are restricted to Men, one to Men or Women, and fifteen to Women, the latter being intended for women who at the conclusion of their Arts or Science Course will proceed to Medicine.

A Berry Research Scholarship in Chemistry, of the value of £80, tenable for one year, will be open to competition by students of either sex at the close of the Winter Session.

A Hall of Residence is provided for Women Students.

Two Degrees in Science are conferred by the University of St. Andrews, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.), and Chemistry is also included in the curriculum for the M.A. Degree; the regulations will be found in the "University Calendar."

Lecture Courses.

Two distinct Courses of Lectures are given, each comprising at least one hundred meetings of the class.

First Year's Course.—This Class meets at 11 o'clock on five days in the week. The introductory lectures treat of the Nature of Chemical Action, the Classification of Substances into Elements and Compounds, the Phenomena of Oxidation, and the Composition of Air and Water. The Laws of Chemical Combination and the Atomic Theory are next discussed, after which the more commonly occurring elements and inorganic compounds are described systematically. Elementary Organic Chemistry is also included in the Course.

The chemistry of manufactures is referred to only cursorily; special attention, on the other hand, is given to those parts of the science which are of general educational value, and as much of the theory of chemistry is introduced as is compatible with elementary treatment.

This course of instruction is intended to meet the requirements of the M.A., First Science, and M.B., Ch.B. Exams., so far as Theoretical Chemistry is concerned.

Second Year's Course.—The first part of the Course is devoted to Organic Chemistry, and the second part to General and Physical Chemistry, the instruction in general being such as is required for the Final Science Exam.

Certificates are awarded on the results of examinations, and the "Forrester Prize" of about £10 is awarded to the best Student of the year.

Fee for the Session, for each Course, £4 4s.

Practical Chemistry.

The Laboratory is open daily from 9 a.m. to 4 p.m., except on Saturdays, when it is closed at 1 p.m. The work pursued in the Laboratory comprises:—(1) The performance of experiments illustrative of the Principles of Inorganic and Organic Chemistry; (2) Qualitative and Quantitative Analysis. Each student pursues an independent course of study under the supervision of the Professor or Demonstrator, the nature of the work varying with the proficiency of the student and the particular object he may have in view. Suitable courses of instruction in Practical Chemistry are provided for candidates for the Examinations in Arts, Science, and Medicine.

The fee for the Ordinary Course of Practical Chemistry is £3 3s, and for the Advanced Course £5 5s.

A special Research Department has been instituted by the University, the laboratories of which are open to

students who give proof of their capacity of conducting chemical investigation.

QUEEN'S COLLEGE, BELFAST.

Professor—E. A. Letts, Ph.D., D.Sc., F.R.U.I., F.R.S.E., &c.

I.—*Chemistry.*—The lectures are delivered at 3 p.m., on the first five days of each week, and terminate at the end of March The course is divided into three parts:—(1) Chemical Philosophy; (2) Inorganic Chemistry; (3) Organic Chemistry. Fee, £2.

II.—*Practical Chemistry.*—In this course the Students are instructed in the general methods of conducting Chemical Analyses. Fee, £3.

III.—*Laboratory Pupils.*—The Chemical Laboratory is open from November until the end of March, and from May 1st until the third week of July, on the first five days of the week, from 10 a.m. until 4 p.m. Students are admitted as working pupils on payment of a fee of £5 for the first period, or of £3 10s. for the second period (or for a single term).

The new Chemical Laboratories are now open, and are provided with all modern appliances. Special facilities are offered to those engaged in Research work.

Scholarships.—The following College Scholarships are awarded specially in connection with the schools of Chemistry and Physics:—Senior Scholarships in Chemistry alone awarded annually of £40, and tenable for one year. Andrews Studentship in Chemistry and Physics, value about £80 annually, and tenable for two years. 1851 Exhibition Scholarships: One of these Scholarships has hitherto been placed at the disposal of the College every two years, of the annual value of £150, tenable for two or under special conditions for three years.

The following Scholarships, &c., of the Royal University of Ireland are awarded in the same group of subjects (Chemistry and Physics):—At the B.A. Degree examination, First-class Exhibitions of £42 each and Second-class Exhibitions of £21. At the M.A. Degree examination, a Studentship of £100 per annum, tenable for three consecutive years. Also a Junior Fellowship, tenable for four years, of the annual value of £200.

QUEEN'S COLLEGE, CORK.

Professor—Augustus Edward Dixon, M.D.

Demonstrator—John Taylor, M.Sc.

The College Session will commence on October 15th, 1907, and end on June 13th, 1908. All classes are open to male and female students.

The courses in Chemistry, though designed primarily to meet the requirements of candidates proceeding to the Examinations in Arts, Medicine, and Engineering of the Royal University of Ireland, of the Medical Licensing Bodies of Dublin and Edinburgh, and of the Pharmaceutical Society of Ireland, can be arranged specially as required, so as to render them suitable to any particular course of study. The following courses are provided:—

Systematic Chemistry.

I. General Lecture Course; three terms. Inorganic Chemistry, Elementary Organic Chemistry, and Chemical Philosophy.

II. Advanced Organic Chemistry, and Chemical Philosophy.

Practical Chemistry.

III. Winter Course of Practical Analytical Chemistry; commencing early in January, 1908.

IV. Summer Course of three months' duration, for students of Medicine; ending about the third week in June.

V. Course for Pharmaceutical Students; held during the second and third terms.

Laboratory Work.

VI. The Chemical Laboratory is open daily from 10 to 4 o'clock, except on Saturdays, to Students entering for Special Courses of practical work in General Inorganic Chemistry, Qualitative and Quantitative Analysis, Organic Chemistry, or for the purpose of Original Investigation.

Scholarships, &c.—In addition to the Class Prizes given at the Sessional Examinations, the College awards a Senior Scholarship of the value of £40, for Chemistry and Physics (either of which may be taken as a limited course), and numerous Junior Scholarships in Arts, Medicine, and Engineering, of which chemistry forms a part, value from £20 to £24 each, annually. The Royal University of Ireland also offers Exhibitions in Chemistry and Physics, First-class value £42, and Second-class value £21, together with other prizes, *e.g.*, a Studentship of £100 per annum, tenable for three years; and the 1851 Exhibition Scholarships, value £150, tenable for two, and, under certain circumstances, for three years, have from time to time been placed at the disposal of the College.

Full particulars as to Lectures, Fees, Scholarships, Exhibitions, &c,, are contained in the Regulations extracted from the College Calendar, which will be supplied on application to the Registrar.

QUEEN'S COLLEGE, GALWAY.

Professor—Alfred Senier, Ph.D., M.D., F.I.C., F.C.S., M.R.I.A.

Demonstrator—Arthur Compton, B.A.

Research Assistant—Percy C. Austin, M.A.

The Session commences in October and ends in June.

Chemistry is studied by attendance at Lectures, by work in the Laboratories, and by the use of the College Library. The Courses in the several faculties are arranged with a view to the requirements of the Royal University of Ireland, but are adapted also to those of other Universities and licensing bodies.

Lecture Courses. Faculty of Arts.—1. Second year's Course, Inorganic and Organic, and the Elements of General Chemistry. 2. Third year's Course, Advanced Organic Chemistry. 3. Fourth year's Post-Graduate Course, Advanced General Inorganic and Organic Chemistry. *Faculty of Medicine.*—First year's Course, Inorganic and Elementary Organic Chemistry. *School of Engineering.*—First year's Course, Inorganic Chemistry.

Laboratory Courses. Faculty of Arts.—1. Second year's Course, Exercises in Inorganic Qualitative Analysis. 2. Third year's Course, Quantitative Analysis and other experiments to suit the requirements of individual Students. 3. Fourth year's Post-Graduate Course, Advanced Quantitative Analysis, Organic and Inorganic Preparations, and determination of their Physical and Chemical characters. 4. The Laboratories are also open to Students for work in other branches of Chemistry. *Faculty of Medicine.*—1. Second year's Course, Inorganic and Organic Elementary Qualitative Analysis, and the Chemical Examination of Urine. *School of Engineering.*—1. Second year's Course, Inorganic Qualitative Analysis.

A Scholarship in Chemistry is offered for competition each year of the value of £40, and Chemistry enters into the subjects required for numerous Scholarships in Arts, Medicine, and Engineering. The Royal Commissioners for the Exhibition of 1851 offer every two years a Science Research Scholarship of £150 per annum. This Scholarship has already been held by five Chemistry Students of this College.

For details as to Fees, Regulations as to Scholarships, and other particulars apply to the Registrar, from whom the Calendar, published in December, and the Extracts from Calendar, published in advance in July, may be obtained.

ROYAL COLLEGE OF SCIENCE, DUBLIN.

Dean of Faculty and Professor of Chemistry—W. N. Hartley, F.R.S., D.Sc.

Lecturer on Organic Chemistry—Alphonsus O'Farrelly, M.A.

Senior Assistant—J. Holms Pollok, D.Sc.

Junior Assistant—G. G. Leonard, A.R.C.Sc.I.

The Royal College of Science supplies, as far as practicable, a complete course of instruction in Science applicable to the Industrial Arts, and is intended also to aid in the instruction of teachers for the local Schools of Science.

Diplomas are awarded in the Faculties of Engineering (Mechanical and Electrical), Applied Chemistry, and Agriculture. If accompanied by a certificate from the Professor of Chemistry, the Diploma of Associate of the Royal College of Science in the Faculty of Applied Chemistry is recognised by the Council of the Institute of Chemistry of Great Britain and Ireland as qualifying candidates for admission to the practical examinations of the Institute.

The instruction in Chemical Science includes (1) General Chemistry; (2) Organic Chemistry, Elementary and Advanced; (3) Analytical and Experimental Chemistry; (4) Instruction in Chemical Research.

Fees payable by Non-Associate Students:—£2 for each separate Course of Lectures. For Analytical Chemistry and Research—£5 for three months; £9 for six months; £12 for the entire session. For Assaying—£5 for three months; £9 for six months. £12 for the entire session.

There are four Royal Scholarships of the value of £50 each yearly, with Free Education, including Laboratory Instruction, tenable for two years; two become vacant each year; they are awarded on the results of their examinations to Associate Students, not being Royal Exhibitioners, who have been a year in the College.

A limited number of Scholarships in Science and Technology are competed for each year. These Scholarships include free education for the full Associateseip Course of three years and maintenance allowance of a guinea a week during the Session.

CHEMICAL LECTURES, CLASSES, AND LABORATORY INSTRUCTION.

City and Guilds of London Institute for the Advancement of Technical Education.—The operations of the City and Guilds of London Institute are divided broadly into four branches: the educational work of three London Colleges, and of the Technological Examinations. Programmes of the London Colleges may be had on application to the Head Office of the Institute, Gresham College, Basinghall Street, London, E.C., or from the respective Colleges. The Technological Examinations (Examinations Department, Exhibition Road, S.W.), are conducted once every year at various centres throughout the kingdom. The Programme of the College, containing full particulars of the conditions of entrance, fees, and courses of instruction, may be had on application. *City and Guilds Central Technical College, Exhibition Road.*—Professor of Chemistry, H. E. Armstrong, Ph.D., F.R.S. The object of this Institution is to give to London a College for the higher technical education, in which advanced instruction shall be provided in those kinds of knowledge which bear upon the different branches of productive industry, whether Manufactures or Arts. The main purpose of the instruction given is to practically demonstrate the application of different branches of science to various manufacturing industries. In order that this instruction may be efficiently carried out, the Institution, in addition to the lecture theatres and class rooms, is fitted with laboratories, drawing offices, and workshops; and opportunities are afforded for the prosecution of original research, with the object of the more thorough training of the students, and for the elucidation of the theory of industrial processes. The courses of instruction are arranged to suit the requirements of—1. Persons who are training to become Technical Teachers; 2. Persons who are preparing to enter Engineers' or Architects' offices, or Manufacturing works; 3. Persons who desire to acquaint themselves with the scientific principles underlying the particular branch of industry in which they are engaged. The Matriculation Examinations begin on Tuesday, September 17th, and the Winter Session opens on Tuesday, October 1st. *City and Guilds Technical College, Finsbury.*—Professor of Chemistry, Raphael Meldola, F.R.S. The operations of the Technical College, Finsbury, are divided into two distinct portions: Day Classes for those who are able to devote one, two, or three years to systematic technical education; Evening Classes for those who are engaged in industrial or commercial occupations in the daytime and who desire to receive supplementary instruction in the application of Science and of Art to the trades and manufactures in which they are concerned or employed. Each Professor is assisted by Demonstrators. Besides these there are Lecturers and Teachers in special subjects. An examination for the admission of Students will be held at the College on Tuesday, September 17th. Session begins October 1st. *South London Technical Art School.* — Classes in Modelling, Design, Drawing and Painting, House Decoration.

City of London College, White Street, Moorfields.—I. S. Scarf, F.I.C., F.C.S., and Assistants. Courses of Saturday and Evening Lectures and Laboratory Practice in Chemistry and Physics, open to Students of both sexes. Day Commercial School, commences Sept. 16. Session commences September 30th.

Battersea Polytechnic.—Principal, Mr. S. G. Rawson, F.I.C. Inorganic, Organic, and Technological Chemistry, Mr. John Wilson, M.Sc. (Vict.), assisted by Mr. John L. White, D.Sc., Mr. J. Hart Smith, A.R.C.Sc., F.I.C., and others. Session opens Sept. 30. Complete courses of Instruction are given in Chemistry (Inorganic and Organic), together with Physics, Electricity, Engineering subjects, German, &c., for intending technological and works chemists. Certain of the Courses (Day and Evening) are recognised by the University of London in preparation for the B.Sc., for which examination (Pass and Honours) complete courses of instruction, under recognised teachers, are provided. Special Evening Courses in Paper and Pulp Testing, Paper Making, Gas Analysis, Assaying, Oils, Fats, Soap and Candle Manufacture.

Birkbeck College, Breams Buildings, Chancery Lane.—Chemistry Courses conducted by Dr. Alex. McKenzie prepare for various Examinations, the B.Sc. and M.B. Degrees of the London University, Conjoint Board, Pharmaceutical Examinations, Board of Education, &c. This Institution, which has now completed eighty-four years of educational work, will commence the new Session on Monday, September 30, when G. G. Chisholm, Esq., M.A., B.Sc., will give the Opening Address, at 7.30 p.m. The Day and Evening courses of study include Chemistry, Physics, Botany, Zoology, Geology, Mathematics, Latin, Greek, Modern Languages, Economics, Geography, Logic, and various branches of Law. Courses conducted by recognised teachers of the University provide for the Examinations of the University of London, in the faculties of Arts, Science, Commerce, and Law. The Report for the last session shows that during the year 104 students passed some examination of the University of London, while a large number gained successes at various public examinations. The College has added considerably to its appliances in recent years, and the Physical, Chemical, Biological, and Metallurgical laboratories are very thoroughly equipped. Courses in Mining, Metallurgy, and Assaying are given both in the day and evening. The Modern Language classes include Italian and Spanish, as well as French and German. The College possesses a School of Art, open both day and evening. The Calendar supplies detailed information respecting the Courses of Study, Examinations, Studentships, &c.

Borough Polytechnic Institute, 103, Borough Road, S.E. — Chemistry: Evening Lectures and Laboratory Work in Inorganic and Organic Chemistry (Session fees, per course, 10s. to 15s.); Electrochemistry,

lecture on Wednesday evenings; Dr. F. Mollwo Perkin, assisted by H. D. Law, B.Sc., and C. T. Bennett, B.Sc. Electricity and Magnetism, and Electro-technics: Evening Lectures and Laboratory Work (Session fees, per course, 10s. to 15s.), Dr. J. Henderson, assisted by H. Saunders. Special Evening Courses on Painters' Oils, Colours, and Varnishes. Session opens Monday, Sept. 23.

SOUTH WESTERN POLYTECHNIC, Chelsea, S.W.—Principal, Sidney Skinner, M.A. Head of the Chemical Department, J. B. Coleman, A.R.C.S., F.I.C. Day and Evening Courses in Theoretical and Practical Chemistry and several branches of Applied Chemistry including Metallurgy, Assaying, Photography, &c. Systematic Courses are held for the Matriculation, Inter. Sci., and B.Sc. Examinations (Pass and Honours) of the University of London. The Day Course in Chemistry is of three years' duration; it gives a thorough training to those who wish to become Consulting or Industrial Chemists. Prospectus of Day and Evening Classes may be obtained from the Secretary, 1d., by post 4d.

EAST LONDON COLLEGE, Mile End Road, E.—Chemistry: Professor, J. T. Hewitt, M.A., D.Sc., Ph.D.; Assistants, Clarence Smith, D.Sc., and F. G. Pope, B.Sc. Lectures and Practical Classes are conducted in the Day Technical College, the regular College Course being three years. The work of the first year corresponds with the requirements of the Int. Sci., Lond., that of the next two years with the degree examination, B.Sc. (Honours and Pass). Special attention is given to work for the Honours Examination and research. Evening Classes for London University Degrees are also held. The College re-opens October 1st.

UNIVERSITY TUTORIAL COLLEGE, 32, Red Lion Square, Holborn, W.C.—This Institution contains large Laboratories for Chemistry, Physics, Geology, and other subjects. Classes are specialised for Examinations of London University, but students may take up work for any Examination. The special feature of the College is that work goes on all the year round, thus affording students residing in the Country an opportunity of doing practical work during their Vacations.

SIR JOHN CASS TECHNICAL INSTITUTE, Jewry Street, Aldgate.—Principal, Charles A. Keane, M.Sc., Ph.D., &c., assisted by H. Burrows, Ph.D., F.I.C., Arthur R. Ling, F.I.C., R.S. Willows, D.Sc., and C. O. Bannister, A.R.S.M. Evening Classes in Chemistry, Metallurgy, Brewing and Malting, Physics, and Mathematics, designed to meet the requirements of those engaged in Chemical, Metallurgical, and Electrical industries, and also in other departments of Science and Art. Practical laboratory work. Courses of Instruction in Glass Blowing, by A. C. Cossor. Classes begin September 23. Full details may be obtained on application, or by letter to the Principal.

THE INSTITUTE OF CHEMISTRY OF GREAT BRITAIN AND IRELAND.—The Institute of Chemistry was founded in October, 1877, and incorporated by Royal Charter in June, 1885, (i.) to promote the better education of persons desirous of becoming public and technical analysts and chemical advisers on scientific subjects; (ii.) to examine Candidates, and to grant certificates of competency; and (iii.) to elevate the profession of Consulting and Analytical Chemistry by setting up a high standard of scientific and practical proficiency and by insisting on the observance of strict rules in regard to professional conduct. *The Studentship.*—Every Candidate for admission to the Studentship is required to produce evidence that he is at least seventeen years of age, and that he has passed a Preliminary Examination in subjects of general education, recognised by the Council of the Institute. He must also show that, at the time of making application for registration, he is working at a College or University approved by the Council, or in the laboratory of a Fellow of the Institute, with the object of adopting the profession of Analytical and Consulting Chemistry. *The Intermediate Examination.*—Candidates for admission to the Intermediate Examination are required to produce evidence (I.) of having passed an approved Preliminary Examination in subjects of general education; (II.) of having regularly attended systematic day courses, in a College or University recognised by the Council, during at least three academic years, in theoretical and practical Chemistry, and courses in Physics, Mathematics, and one of the following subjects, in accordance with the Regulations of the Institute: (i.) Advanced Mathematics; (ii.) Mechanics and Chemical Engineering; (iii.) Metallurgy; (iv.) Geology and Mineralogy; (v.) Physiology; (vi.) Bacteriology; and (III.) of having satisfactorily passed the Class Examinations in all the subjects required to be taken. As an alternative in the matter of training (II.), a candidate may take two years' training in a recognised Institution as indicated above, and work systematically for two other years in the laboratory of a Fellow of the Institute. A Candidate who has taken a Degree in Science (including Inorganic and Organic Chemistry, and Physics in the Degree Examination, Mathematics having been also passed in at either the Final or Intermediate University Examination) in a University recognised by the Council, is eligible for admission to the Intermediate Examination of the Institute. Holders of certain Degrees or Diplomas are exempt from passing the Intermediate, and, by virtue of their qualifications, are eligible for admission to the Final Examination direct. *The Final Examination for the Associateship (A.I.C.).*—Any Candidate who has passed the Intermediate Examination of the Institute, or who is entitled to claim exemption from passing the Intermediate Examination, is eligible for admission to the Final Examination. *Fellowship (F.I.C.).*—For admission to the Fellowship, an Associate is required to have been registered for three years, and to have been continuously engaged during that period in the study and practical work of Applied Chemistry in a manner satisfactory to the Council. Full particulars are given in "The Book of Regulations for the Admission of Students, Associates, and Fellows," which may be obtained (Price One Shilling) of Messrs. Blundell, Taylor, and Co., 173, Upper Thames Street, London, E.C.

IMPERIAL COLLEGE OF CHEMISTRY AND PHARMACY, 49 and 51, Imperial Buildings, Ludgate Circus.—Mr. F. Davis, B.Sc. An especial course of instruction is given at this College in Pharmacology and Therapeutics, *re* the Institute of Chemistry Examination. Students attending the College visit technical works.

THE POLYTECHNIC, 309, Regent Street, W.—University of London Preparation Classes. Chemistry: R. A. Ward, F. E. Weston, B.Sc., F. Harvey, W. H. Collier, and H. R. Ellis, B.Sc.

BLACKBURN MUNICIPAL TECHNICAL SCHOOL.—Chemistry: Mr. Robert H. Pickard, D.Sc.(Lond.)., &c., assisted by Messrs. Jos. Yates, W. O. Littlebury, F.I.C., and Jos. Kenyon. Session opens Monday, Sept. 23. Full details of the Classes are given in the "Students' Handbook," which may be had at the Institution (price 1d., by post 3d).

REDRUTH SCHOOL OF MINES, CORNWALL.—Principal, Howard C. Ridding, A.R.S.M., F.I.C., assisted by a staff of Mining Engineers and Mine Surveyors Courses of Practical and Theoretical instruction are given in Inorganic Chemistry, Assaying, Mineralogy, Blowpipe Analysis, Mine Surveying, Geology, Principles of Mining, Ore Dressing, Mechanical Engineering, &c., for intending Assayers, Mineral Chemists, Mining Engineers, and Surveyors. Shorter Courses are also held in the above-named and cognate subjects to meet the requirements of those having a limited time at their disposal and Prospectors. Practical instruction in Mining given at the Basset Mines, Ltd. Syllabus on application to the Registrar. Session commences Wednesday, Sept. 11.

COUNTY TECHNICAL LABORATORIES, Chelmsford.—Agriculture: B. W. Bull, N.D.A. Analyst: V. H. Kirkham, B.Sc., A.I.C. Biology: C. A. Ealand, B.A., R. Robson,

B.Sc. Chemistry and Physics: A. Neville, B.Sc., A.I.C., H. T. Cranfield, Miss K. Jackson.

LEEDS INSTITUTE: TECHNICAL SCHOOL, Cookridge Street, Leeds.—Head Master, R. E. Barnett, B.Sc. (Lond.), A.R.C.S. Evening Classes are held in over sixty subjects of Science and Technology, among which are:—Chemistry (Inorganic and Organic), Chemical Calculations and Principles of Analysis, by Mr. R. E. Barnett, B.Sc., A.R.C.S., Mr. J. B. Murray, Mr. A. McFarlane, and Mr. O. F. Kirby, M.A., B.Sc.; Metallurgy (Theoretical and Practical) and Iron and Steel Manufacture, by Mr. B. A. Burrell, F.I.C., F.C.S.; Gas Manufacture, by Mr. W. E. Pettigrew; Oils and Fats, by M. W. Dillon; Magnetism and Electricity, Practical Physics, &c., by Mr. J. E. Tindall, B.A., B.Sc.; Botany, Lectures and Practical Work, by Mr. N. Walker; Photography, by Mr. S. E. Bottomley. Fees: from 7s. 6d. per session. Group courses arranged for Students engaged in Chemical Industries. Session commences Sept. 17th. Prospectuses of various Classes free on application to the Head Master, or to Mr. James Graham, Secretary for Higher Education, Calverley Street, Leeds.

CITY OF LEEDS HIGHER EDUCATION DEPARTMENT.—Courses of Evening Classes have been arranged for the Minor Examination of the Pharmaceutical Society, in which the whole Syllabus will be covered in three Winter Sessions. Chemistry: Mr. S. Parrish, B.Sc., A.R.C.S., Chief Lecturer in Chemistry, Central High School, and Mr. J. B. Murray. Botany: Mr. Norman Walker, Assistant Lecturer in Botany, Leeds University. Pharmaceutics: Mr. J. H. Gough, Ph.C., F.C.S., Demonstrator in Materia Medica and Pharmacy, Leeds University. Full particulars from Mr. James Graham, Secretary for Higher Education, Education Offices, Leeds.

MUNICIPAL SCHOOL OF TECHNOLOGY, Sackville Street, Manchester.—This building occupies an area of 68oo square yards and is six floors in height. Its equipment is on a scale of great magnitude. It comprises laboratories and workshops for Mechanical, Electrical, Sanitary and Hydraulic Engineering, for the Textile industries, for Photography, Collotype and Photo-mechanical processes, for the Letterpress and Lithographic industries, and for the industries included within the scope of Architecture. The provision for the teaching of Chemistry, as might be expected in a district where the Chemical industries are important, is of an exceptionally complete character. It comprises, in addition to ample accommodation for pure Chemistry, laboratories for Metallurgy, Brewing, Bleaching, Dyeing and Printing, Paper-making, and Electro-chemistry. The Bleaching, Dyeing, Printing and Finishing, and the Paper-making industries are in addition extensively equipped in a separate building with machinery and appliances on an industrial scale. A Brew-house is also equipped on the low gravity principle, with a plant of four bushel capacity. The School is now established as the Faculty of Technology in the University of Manchester, and students of the School fulfilling the conditions can proceed to the Degrees of Bachelor and Master of Technical Science (B.Sc. and M.Sc. Tech.). Entrance Examinations, Sept. 9—11. Session commences Sept. 16.

WOLVERHAMPTON MUNICIPAL SCIENCE AND TECHNICAL SCHOOL.—Inorganic and Organic Chemistry, Mr. W. Whitehouse, F.C.S.; Physics, Messrs. W. Whitehouse and A. T. Harrison, B.Sc.; Botany, Mr. Sidney Phillips, Ph.C. Day Classes in Chemistry, and Evening Classes in Chemistry, Physics, Botany, French, &c. Special arrangements are made for the requirements of Pharmaceutical and Medical Students. Session commences Monday, Sept. 16th. For other particulars and programme, apply Mr. G. F. Chell, Secretary.

ERRATA.—P. 98, col. 1, line 3 from bottom *read* "reference and free from hypothesis." P. 107, col. 2, line 33 from bottom, *for* "Borides" *read* "Bromides."

GRIFFIN'S STUDENTS BOOKS.

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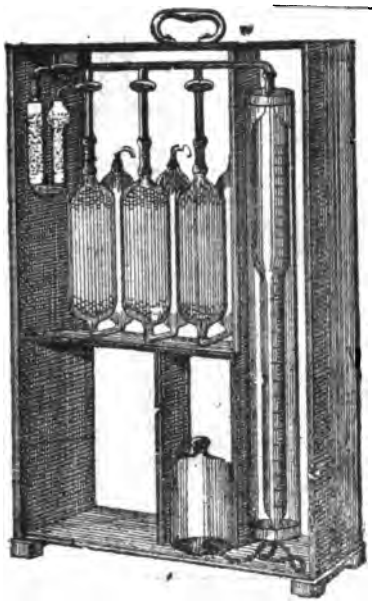

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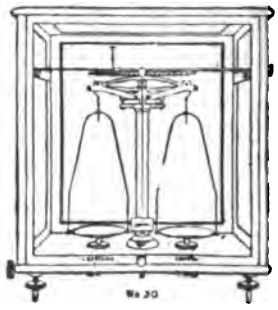

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THE ATOMIC WEIGHT OF RADIUM.

By Mdme. CURIE.

THE determination of the atomic weight of radium which I published in 1902 (*Comptes Rendus*, July, 1902) was carried out with 9 centigrms. of radium chloride. Fresh processes having since then furnished some decigrms. of practically pure chloride, I have subjected them to purification, which enabled me to obtain 4 decigrms. of perfectly pure radium chloride, and to determine the atomic weight of radium under far better conditions than before.

[NOTE.—I have already had an opportunity of thanking those who, in the first years of our researches on radioactive substances, gave the assistance which is indispensable in such costly experimental work (Mdme. Curie, Thèse de Doctorate). I am glad to take this opportunity of thanking those who have now enabled me to obtain a relatively large amount of radium salt. The best radium mineral (the residue of Joachimsthal pitchblende after the extraction of the uranium) being in great demand, the Austrian Government, at the suggestion of the Vienna Academy, has consented to reserve to us the right of buying 10 tons of this mineral. Baron E. de Rothschild has kindly provided the funds necessary for buying this amount. Finally, the treatment of this mineral has been, and is still being, carried out at the factory of M. Armet de Lisle, who has most generously defrayed the cost, and who has also kindly allowed us to make use of his factory for studying radio-active substances.]

The purification processes consisted as before in fractional crystallisation in water containing hydrochloric acid, or in fractional precipitation of the aqueous solution by alcohol. The progress of the fractionation was controlled by photographs of the spark spectra, obtained with the spectrograph which formerly belonged to Demarçay. It is convenient to compare the relative values of the lines 4554·4 of barium and 4533·5 of radium. These lines, which are very close together, are very suitable for comparison. The line 4554·4 is the strongest in the barium spectrum, and the line 4533·5 is one of medium importance in the radium spectrum.

When the purification was stopped, the strongest barium line was still faintly visible near the other. Its complete elimination seemed to be very difficult with the quantity of material I had at my disposal. Nevertheless, I shall shortly show that the salt was very pure.

I was confronted with one difficulty during this work. When a clear solution of a radium salt is evaporated in a dish or glass, the dry salt obtained is not generally completely soluble in water, but leaves a residue. I have found that this residue is partly due to the formation of radium sulphate, in consequence of the presence of traces of sulphuric acid in the reagents (traces which could only be detected by barium salts after the concentration of the reagents), and partly to the slow action of the radium salts on the vessels. I therefore decided to prepare specially all the reagents employed. The water was distilled in a platinum still, and received and kept in a platinum flask; this water was used to prepare the hydrochloric acid, which was also kept in a platinum flask. The nitric acid, alcohol, and silver nitrate were also purified. It is not possible to let the radium chloride crystallise in presence of hydrochloric acid in a platinum dish, because it has considerable action on the latter. But if the clear solution is allowed to crystallise rapidly in a porcelain dish, crystals are obtained, which, after being dried, dissolve in the purified water without residue, and hence can be used to determine the atomic weight.

The method employed for this determination was the same as before. It consists in estimating as silver chloride the chlorine contained in a known weight of anhydrous radium chloride. According to my earlier experiments, which were confirmed by new observations, radium chloride, which has just been prepared, loses its water of crystallisation when it is heated in a drying oven above 100°, and its weight is quite constant when it has been subjected for half-an-hour to a temperature of 150°.

The weighings were performed with a Curie's aperiodic balance with direct reading for weights below decigrms. This rapid balance is accurate to one-tenth of a m.grm., and takes only ten seconds to reach its position of equilibrium. The weighing of the radium chloride is more difficult than that of the silver chloride, because the former salt absorbs water-vapour rather quickly; it is therefore essential to let it cool in a desiccator with phosphoric anhydride before weighing, and not to re-commence weighing until after it has been again placed in the drying oven, even if the cage of the balance contains desiccating substances.

After each estimation the radium is present as nitrate with silver nitrate. The silver is eliminated by hydrochloric acid, and the nitric acid by repeated crystallisation in presence of hydrochloric acid.

The following table gives the numbers obtained in three consecutive experiments, and the atomic weights P deduced from them, assuming that radium is a divalent metal, and that the atomic weights of silver and chlorine are—

$$Ag = 107{\cdot}8,\ Cl = 35{\cdot}4.$$

Radium chloride.	Silver chloride.	P.
0·4052	0·3906—0·00006	226·35
0·4020	0·3879—0·00006	226·04
0·39335	0·3795—0·00006	226·15

Weight of filter ash = 0·00006.

The weighings of the two chlorides are considered to be exact to about one-tenth mgrm. These three experiments, which agree very closely, give for the atomic weight of radium the mean value 226·18.

The experiments, performed in 1902 with very pure radium chloride, gave less concordant results and a mean of 225. The spectrum of the salt used recently shows a rather greater degree of purity, but the difference of about one unit in the atomic weight could not be ascribed to this cause. I performed a control experiment as follows:—I prepared a solution of some mgrms. of pure 1907 salt, and added to it a small quantity of a titrated solution of barium chloride. The amount of barium salt in the mixture was 0·61 per cent. In the spectrum of this salt a great increase of the intensity of the barium spectrum is shown, whereas the change of atomic weight, calculated from the known addition of barium chloride, is only 0·7 unit. From the examination of the spectra it is clear that the difference between the numbers obtained in 1902 and in 1907 should be attributed only to the inferior accuracy of the experiments performed with only 9 centigrms. of radium salt and with less pure reagents.

The above experiment also proves that the spectral reaction of barium in presence of radium is very sensitive, and that the radium chloride which was used for the determination must be very pure. It certainly does not contain 0·1 per cent of barium chloride.

I therefore conclude from these experiments that the atomic weight of radium is 226·2 (Ag = 107·8, Cl = 35·4) with a probable error of less than half a unit.

If the values Ag = 107·93, Cl = 35·45 are adopted, the value is Ra = 226·45.

The reproduction of the spectra and the description of the details of the experiments will appear in the journal *Le Radium.—Comptes Rendus*, 1907, vol. cxlv., p. 422.

VALENCY.*

By A. WERNER.

Introduction.

The development of the doctrine of valency shows that our present ideas of valency have resulted from the endeavour to obtain a numerical expression for those intramolecular affinity relations which, on the basis of chemical reactions, are to be regarded as the cause of the linking together of the atoms in the molecule. Thus, we must take as the basis of our conceptions of valency those structural and constitutional formulæ in which the affinity relations between the atoms are represented graphically by strokes. The number of the strokes in each case shows with how many other atoms the atom of any given element exists in so-called chemical combination, and thus determines the combining value of the atoms. This combining value is also called the valency of the elements. The valency was first regarded as a number of constant magnitude, characteristic of the atom of each element, and it was said to show with how many other elementary atoms it could combine. This view had, however, to be abandoned, for reasons to which I shall return later, and it was then thought that valency is a relative number depending upon the nature of all the atoms in combination with one another. Thus the idea of valency lost its original precise form, for owing to the great number of elements there were so many possibilities of combination for each atom that the valency of the atoms of an element could be represented by very different numbers. The chief object of the idea of valency—to afford a more settled basis for the representation of constitutional formulæ—was in consequence lost sight of. In order to preserve as much as possible of the original conception of valency, which had been so very fruitful in the region of the carbon compounds, in which it had chiefly been developed, for ten years attempts were made to compress the constitutional and structural formulæ of all possible compounds into schemes which could in no way fit in with the properties of the compounds. But, finally, it had to be recognised that in this way a corresponding doctrine of the constitution of the inorganic compounds could not be deduced, and hence the final result of these efforts is that the doctrine of valency has been confirmed for the compounds of carbon, but not for those of other elements. In consequence we were obliged to deduce the affinity relations in the molecules of compounds of other elements only from the properties of the compounds in question, paying no regard to the original ideas of valency, and to represent them graphically by suitable structural formulæ. Hence, it appeared that most elements can exhibit atomic linkages which could not be foreseen from the ordinary ideas of valency, and for which no theoretical expression could be deduced from these views. As a consequence, there necessarily arose the need of a comprehensive expression for the linkage power of the atom, a theoretical expression from which those constitutional formulæ which were based upon experimental work, but which could not be explained by the ordinary valency ormulæ, could be deduced. The doctrine of valency is in this state of development at the present time, and recent efforts in this region can therefore be summarised by saying that a search is being made for a general law expressing all the possibilities of linking of the atom.

Recent Attempts in the Region of the Doctrine of Valency.

The final form of this general law is yet to be found, and the great difficulties which oppose the deduction of it in purely chemical ways show at once why we have tried to arrive at the formulation of this general law on another basis than that of the frequently very tedious investigation of constitution. Thus, you know that Abegg, from considerations which he bases upon a special form of the Periodic System of the elements, has tried to construct a general valency law of the elements. And undoubtedly the chemical valency theories which W. Barlow and W. J. Pope have developed from their views on the structure of crystal molecules are also to be regarded from this point of view. All these experiments are of great value, and will certainly help towards the explanation of the problem of valency. I shall now turn my attention to the purely chemical constitutional formulæ and the ideas of valency arising from them.

General Doctrine of Valency.

All the ideas of valency deducible from the experimentally established constitutional formulæ of organic and inorganic compounds can be called the "extended valency theory" as distinguished from those specially deduced from the constitution of organic compounds. At the present time this theory is not simple in character, but it is composed of different heterogeneous views, the internal fusion of which to comprehensive ideas may be regarded as the final aim of the investigation of valency. We shall now proceed to examine into these separate ideas.

a. Direct and Indirect Linkage.—It was formerly generally assumed that two atoms could be connected with one another by chemical affinity only if they were spacially close to one another, *i.e.*, directly bound to one another as it was called. On the ground of recent researches on the constitution of certain groups of inorganic compounds, viz., the metal ammonium compounds and hydrates, it has, however, been found that atoms can be connected with one another by chemical affinity if, in consequence of the interposition of definite atomic groups bound with the atom in question, a spacial juxtaposition is, as it were, mechanically prevented. This is the case with the compounds $[Co(NH_3)_6]Cl_3$, $[Co(OH_2)_6]Cl_3$, &c. In such compounds the ammonia and water molecules form, as it were, an envelope round the central metallic atom, and thus prevent the direct binding of the chlorine atom to it. This kind of atomic linkage we call "indirect linkage." Indirectly bound atoms and groups are distinguished from those directly bound usually by their much greater power of entering into reactions. This may be recognised in the chemistry of the compounds by the fact that these indirectly bound groups can be directly detected in the aqueous solution of the compounds by means of analytical reagents, while this is not the case with directly bound atoms. Thus, there exists a characteristic difference in the behaviour of directly and indirectly bound radicals, which may be demonstrated very strikingly in those cases in which the molecule of the compound contains both directly and indirectly bound groups. This is the case, for example, in the following compounds:—

$$\left[Co^{Cl}_{(NH_3)_5}\right]Cl_2 \text{ and } \left[Pt^{Cl_2}_{(NH_3)_4}\right]Cl_2.$$

Thus, in the freshly prepared aqueous solution of chloropentammino cobalt chloride it has been found that two-thirds of the chlorine is instantaneously precipitated as silver chloride by silver nitrate, while one-third does not give this reaction. Hence, it must be concluded that indirectly bound groups possess the property of appearing as independent ions in aqueous solution, so that this kind of linkage may be called "ionogenic linkage." Groups which are not bound ionogenically even in aqueous solution remain united in complex radicals with the elementary atom to which they are attached, and then appear as complex ions. The difference between directly and indirectly bound groups is of fundamental importance in the consideration of the constitution of inorganic compounds, which is indicated by the fact that the development of the inorganic constitution doctrine already shows that both different kinds of linkages probably appear in all elements. The importance of this difference for the doctrine of valency lies chiefly in the fact that it leads to the following questions, which are independent of one another:—

* Paper forming part of a Discussion on this subject at the Leicester Meeting of the British Association (Section B), 1907.

1. How many atoms can be directly bound with a definite elementary atom?

2. How many atoms and groups can generally be attached to an elementary atom by chemical affinity?

We shall now consider these questions. The first leads to the conception of the co-ordination number, the second to that of valency.

I. *The Co-ordination Number.*

The investigation of the composition and behaviour of an exceedingly large number of compounds has led to the noteworthy result that the maximum number of atoms and groups directly bound with a central atom is in most elements equal to six, and in a small group of elements it is equal to four. Hence, it follows that the power of linkage of the ordinary atom, in so far as direct bindings are concerned, does not exceed a definite limiting value. This limiting value must therefore be regarded as an important fundamental property of the elementary atoms; it is called the co-ordination number. The co-ordination number is thus that number which states the maximum number of atoms with which a definite elementary atom can be directly linked. The co-ordination number for boron, carbon, and nitrogen is four, and for most other elements, including all the heavy metals, &c., it equals six.

From the fact that only a few elements of the first period, and specially those with the smallest atomic volume, possess the lower co-ordination number four, while all others whose co-ordination number can be determined have the same value six, it must be concluded that this number must be independent within wide limits of the affinity value of the elementary atoms. If, however, this is the case, the co-ordination number can be conceived only as a space number, and it is then that number which states how many atoms can be attached to an elementary atom in a first sphere. This conception leads to many deductions which can be established by experiment. Firstly, it is to be emphasised that with the carbon atom, of which the co-ordination number is four, the four groups, according to the hypothesis of van 't Hoff and Le Bel, are symmetrically disposed round it in space. A further confirmation is obtained from the fact that the saturated carbon compounds differ characteristically from the corresponding compounds of other elements in that they are incapable of forming complex compounds by the addition of other molecular components. Thus, carbon tetrachloride forms no chloro salts.

In the elements with the co-ordination number six the symmetrical space position is represented by an opposite arrangement at the angles of an octohedron. This octohedral position leads us to expect for the cases in which the six groups are not identical, *e.g.*, for molecular complexes, two spacially different possible positions, which must manifest themselves as stereoisomers of the compounds in question. This important conclusion has also been experimentally confirmed for three different elements, platinum, cobalt, and chromium. If we therefore regard the co-ordination number as a space number of the atom, very weighty reasons argue in favour of it, and the co-ordination number represents the first sharply defined theoretical expression, which discloses something definite about the linkage power of the atom. But the co-ordination number is also practically of great fruitfulness as a working hypothesis because it allows us to foretell, in compounds in which the co-ordination number of the central atom is not filled up, that by choosing suitable components co-ordinatively saturated types of compouuds must be able to be prepared.

The Doctrine of Valency.

a. The Unit of Valency.—The original view of the cause of the possible intramolecular dependence between two atoms which we call chemical combination was that for each atom a definite number of unalterable single forces (units of valency) must exist, and that the linking between the atoms in consequence of the mutual saturation of these valencies occurs in such a way that each valency of one atom saturates one valency of the other. As now the hydrogen atom in the compounds considered always combined with only one other elementary atom, the hypothesis was put forward that hydrogen generally possesses only one unit of valency. Therefore it was called monovalent, and all elementary atoms or atomic groups which in chemical compounds take the place of one hydrogen atom, were said to be equivalent to it, *i.e.*, monovalent also. Atoms or groups of atoms which replace two atoms of hydrogen are divalent, &c.

This system of valency has been of great service; nevertheless, it no longer satisfies the demands now made upon a comprehensive system of valency. Thus, it takes no account of the fact that in an exceedingly large number of cases certain atoms are not capable of forming linkages with the hydrogen atom, or atoms and groups equivalent to it, but yet can form a whole series of other perfectly stable atomic compounds. For the valencies which produce these last atomic linkages the valency system based upon the valency of hydrogen can give no standard of comparison, and these new valencies were therefore called by a special name. The valencies referred to that of hydrogen were called principal valencies, and those not thus measurable auxiliary valencies. Thus, it was only because the originally used standard of valency, that of hydrogen, could not be applied as the basis of a system of valency including all atomic linkages that this artificial distinction was proposed. The distinction is not based upon the nature of the atomic linkages produced by the different valencies. This is shown by the fact that radicals united to one another by auxiliary valencies are often very much more firmly bound than those held together by principal valencies, so that no constant difference can be demonstrated as regards the stability of the compounds produced by principal and auxiliary bonds.

In many cases it is also quite impossible to decide whether a certain linkage is to be called a principal or auxiliary valency linkage. Two examples will be sufficient to show this, sodium nitroprusside and carbonyl potassium ferrocyanide :—

$$\left[Fe^{NO}_{(CN)_5} \right] Na_2 \text{ and } \left[Fe^{CO}_{(CN)_5} \right] K_3.*$$

It can hardly be stated by which kind of valency the NO and CO groups of these compounds are bound to the iron, chiefly because, as we shall soon see, the question in such cases is much too indefinite.

For purely structural purposes, *i.e.*, for the graphic representation of the atomic linkages, which are to be assumed on the grounds of chemical properties, the distinction between principal and auxiliary valencies is therefore of no significance, and it would be most natural if without distinction we always expressed all linkages simply by a dot or a stroke between the two atoms in question. If, however, the distinction between principal and auxiliary bonds and principal and auxiliary valencies is kept up, it is because it seems necessary, in view of the present transition state of the doctrine of valency, to construct sharply defined partial conceptions which can afterwards serve as the foundation stones of a more comprehensive conception of valency. When therefore it is required to mark a difference between principal and auxiliary bonds it is preferable to denote the first by a line and the second by a dot.

b. The Unit of Valency as an Unalterable Single Force.—Even now the hypothesis that the unit valency is an unalterable single force acting on the atom has many adherents, especially amongst purely organic chemists. This hypothesis has been extended, and the further assumption made that the single force acts at perfectly definite places on the surface of the atom and in definite directions in space. These hypotheses have, however,

* Written $\left[Co^{NO}_{(CN)_5} \right] Na_2$ and $\left[Co^{CO}_{(CN)_5} \right] K_3$, which is obviously a mistake.—*Ed.* C.N.

proved completely unfruitful, and in the region in which they have been more fully worked out, namely, that of the carbon compounds, it has been found that they do not agree with the actual phenomena. To show this from the experimental material would lead us too far to-day. It will be sufficient to remark that the phenomenon of change of valency, the process of racemisation in optically active compounds, the phenomena of transmutation in geometrically isomeric carbon compounds, and, moreover, the behaviour of carbon compounds with one or more so-called double bonds, are either not compatible with these hypotheses, or else can only be made to fit in with it by great straining. For many of these processes these hypothetical conceptions have led to the elaboration of such artificial schemes in the formulations that the unbiassed theoretical explanation of the experimental results has been very detrimentally influenced, and new hypotheses have constantly had to be brought forward to explain the facts. All these reasons must necessarily lead to the abandonment of the hypothesis of the valency unit as a definite individual force.

c. The Valency Number.—According to the original definition the valency number is the property belonging to the atoms of uniting with a definite unalterable number of the atoms of other elements. Kekulé conceived of the valency number in this sense.

Although this conception has the merit of being simple it has, nevertheless, proved untenable. The valencies of the elements have not constant but varying numerical values, and the true nature of valency phenomena will not be understood until a more accurate investigation of the change of valency has proved what factors influence the valency number. We must regard the nature of the elementary atoms bound with one another as the principal factor which determines the change of valency, for it appears that the atom of an element has a different valency according to the nature of the atoms of other elements linked with it. Hence, the important result follows that valency is not a property belonging to the atoms as such, but a relative property which is dependent upon the nature of all the atoms bound with one another. It is further to be noted that very often an element can combine with another in different proportions, *e.g.*, $FeCl_2$, $FeCl_3$, $SnCl_2$, $SnCl_4$, &c. As now the assumption formerly made to explain these different proportions, of a mutual binding of the atoms of the metal, is untenable, on the basis of the molecular magnitude of the compounds in solution, we must admit that an element can exhibit a changing valency towards another definite element. Also the valency appears to vary with the change of definite external factors, such as temperature, pressure, &c., but we cannot discuss these conditions now. An allusion must, however, be made to a phenomenon which is of considerable importance in the consideration of valency relations, namely, the fact that the change of valency is not equally strongly marked in all elements, but in strongly electropositive elements, the metals, and in strongly electronegative, the metalloids, appears most marked, and is exhibited only relatively seldom by electro-neutral elements, such as carbon. Enough has been said to show that the valency relations of the elements are very various, and that hence it would be difficult to regard them all from one general point of view.

The first attempt in this direction, described below, will therefore necessarily be incomplete. But it is hoped that it will show that a solution of the problem is possible.

Development of the Doctrine of Valency from a Single Fundamental Conception of Affinity.

a. Fundamental Hypothesis concerning Affinity.—As the basis for our examination we shall use the assumption that the affinity of the atom does not act in the form of a single definite force, but acts uniformly from the centre towards the surface of the atom. We do not employ hypotheses concerning the shape of the atom, for as the atoms, even in the molecule, must be assumed to be in constant motion, the exact form of them can be of only subordinate importance as compared with the limits of space in which these movements are completed. These space boundaries for simplicity sake we can regard as spheres, and hence in all developments work on the assumption that the atoms are spherical. But this assumption is not necessary for our examination, for we use no hypothesis about the form of the atom for the development of our theory. The assumption has, however, the advantage of making the mechanical picture of the structure of the molecule easier to conceive. Let us now proceed to consider the phenomena of valency in the light of the hypothesis, worked out by us, on the mode of action of affinity.

b. The Affinity Value of the Unit of Valency.—Each elementary atom is characterised by the definite amount of potential energy it contains, of which a certain amount can take effect as chemical affinity, if it encounters another atom. But this amount can vary within wide limits, for it is always dependent upon the nature of the atoms uniting with one another, or, as it is ordinarily expressed, upon the greater or smaller affinity of the elements in question for one another. Each atomic linkage is therefore characterised by the saturation of a definite amount of affinity, the absolute value of which changes in different cases and is dependent upon the nature of all the atoms present in the molecule. The determination of the absolute value of the linking power of the single bonds is at present not within the regions of possibility. At the most, from the behaviour of the compounds, we are enabled to form opinions whether in definite cases the affinity value of the linkages in question is greater or less. These opinions are based on the following considerations:—Usually if a large amount of the affinity contained by an atom has been used, it has at its disposal only a smaller amount of affinity than when this is not the case. Thus, for example, the oxygen atom of the water molecule, H_2O, has less affinity for further atomic linkages than the oxygen atom of the hydroxyl group. And, further, we can generally conclude that the atoms of the elements in atomic combinations which appear as independent molecules, in new atomic compounds will have smaller amounts of affinity to be saturated than in radicals which have no independent existence. As now the atoms of the first kind in the formation of new atomic linkages call into action auxiliary valencies, and those of the last kind principal valencies, we come to the conclusion that the auxiliary valency linkage corresponds to the saturation of a smaller amount of affinity than the principal valency bond. Thus, between principal and auxiliary valencies there exists a gradual difference as regards their affinity value, and the most varied transition steps will be possible between the two. Accordingly, a sharp line of demarcation between principal and auxiliary valencies cannot be drawn. The views developed above on the affinity value of atomic bonds lead to many interesting conclusions which we shall now discuss somewhat more fully.

1. *Electro-compounds.*—Closely connected with the difference in the affinity values of principal and auxiliary valencies is the power of the atoms of elements to form electro-compounds, among which we understand the so-called ionic condition of atoms and radicals. From a chemical valency point of view the electron shows itself to be equivalent to one atom of hydrogen, *i.e.*, it is monovalent. This means that to link an electron to the atom of an element an amount of affinity is necessary of that order of magnitude which corresponds approximately to the formation of a principal valency bond. Regarded from this point of view the ions appear simply as a special case of a chemical compound produced by the so-called principal valency.

2. *The So-called Double Bond.*—We cannot state anything about the maximum amount of affinity which can be used up between two atoms bound together. It seems probable that the amount of affinity satisfied must be greater the greater the amount still at the disposal of the

atom. Hence, if we compare the union of two groups CH_3 with that of two groups CH_2, the two carbon atoms uniting in the second case will saturate a much greater amount of affinity than in the first case. But in no case need the amount saturated by the carbon atom of CH_2 be double that saturated by the carbon atom of CH_3. Hence we obtain a conception of the so-called double bond. This represents a greater amount of affinity than the single, but does not reach the amount of two single carbon bonds. Still unsaturated amounts of affinity are at the disposal of the carbon atoms of the ethylene groups, which causes the well known transformation phenomena of the ethylene bonds, and as these unsaturated amounts of affinity will be at the same time dependent on the nature of the atoms and radicals linked to the carbon atoms, the unsaturated character of the ethylene compounds must be able to vary within wide limits. This is actually the case, as a comparison of tetraphenyl ethylene, ethylene, and fulvenene shows at once. Many other deductions can be made from the consideration of the changing affinity value of the atomic linkages, but it would require more time than is now at our disposal to go into them fully. We shall therefore content ourselves with discussing shortly the question how the valency numbers can be deduced with the aid of our fundamental views on affinity.

c. Deduction of the Valency Numbers from the Fundamental Hypothesis.—According to our fundamental view, a part of the affinity contained by the atom is saturated by each atomic linkage. The number of the atomic linkages which can be formed will therefore be dependent, on the one hand, on the amount of affinity contained in the atom, and, on the other, on the amounts of affinity which have been saturated by linkages. The ratio of these two to one another will determine the valency number. Hence, we must turn to the questions of the amount of affinity contained in the atom and the magnitude of the affinity value of the linkages of the atom.

1. *The Affinity contained in the Atom.*—There can naturally be no question of a determination of the absolute value of the affinity contained in the atom. We must limit ourselves to trying to find out whether the amount of affinity contained by all atoms is the same, or is different with different elements. For this purpose we shall be obliged to determine the power of combination of an element which behaves itself as uniformly as possible towards others, *i.e.*, requires about equal amounts of affinity when forming an atomic linkage. Hydrogen is suitable for this purpose, for it behaves towards the metalloids as a positive element and towards positive elements as a negative element in hydrides, and occupies a mean position with regard to elements with a feebly defined character (carbon, &c.). If now we compare the composition of hydrogen compounds in the different periods of the natural system of the elements, we arrive at the result that the affinity contained in the atom of an element reaches a maximum in the elements which occupy the middle position (carbon), and decreases according to a law towards the electro-chemically strongly defined elements. The periodicity of the valency numbers of the elements for hydrogen is thus to be regarded as a consequence of the different amounts of affinity contained in the atoms, and the corresponding phenomena in regard to the alkyl compounds are to be ascribed to the same cause. The valency relations resulting from the composition of compounds with distinctly positive or negative elements are to be regarded quite differently. In these cases the affinity values of the atomic linkages, which vary within wide limits, play a great part, as I shall now try to show.

2. *The varying Affinity Value of the Linkages of the Atom as a Cause of the Valency Number.*—Carbon as regards its character takes a middle position between the metals and the metalloids, like hydrogen, and hence it behaves uniformly towards both groups of elements. This analogy explains why the valency numbers of most elements for carbon harmonise with those of the elements for hydrogen, and also why there is a far-reaching agreement between the valency of carbon for hydrogen and that for other elements. But these simple relations in valency phenomena carbon owes only to its peculiar position as regards the other elements, and this is clearly shown by the fact that we meet with essentially complicated valency relations when we pass to elements with electro-chemically more decided characters. This is shown by nitrogen, which is trivalent towards chlorine and pentavalent towards oxygen, while different views are held concerning its valency in the ammonium compounds. And the nearer we approach towards the first and last members of the periods of the natural system, the more intricate are the valency relations, which finally become almost chaotic. The facts now show that in the formation of compounds of allied elements small amounts of affinity are saturated, but for the formation of compounds of chemically very different elements, on the contrary, large amounts are used up. As now the amount of affinity contained by the atoms of the elements is always the same, it is to be expected that in the formation of the former high, and in the formation of the latter, on the contrary, lower valency values will be revealed. This is also the case; for in the compounds of the metals with one another (alloys, amalgams, &c.), and in the compounds of metalloids with metalloids (oxides, &c.), actually high valency numbers appear, and in the compounds of the metals with the metalloids, on the contrary, lower values. Unfortunately, I cannot here discuss these relations more fully, and must also refrain from entering on other questions of the valency theory, *e.g.*, the maximum valency number, the change of valency, &c. The developments here described only serve to lay the foundation of the view that a fuller investigation of the valency phenomena of the elements must be based on a general doctrine of affinity.

THE VAGARIES OF BERYLLIUM.*

By CHARLES L. PARSONS.

As it has become a custom in the American Chemical Society for the Chairmen of the various Sections, into which the Sessions of the General Meetings are divided, to present an Address upon some branch of their work in which they are especially interested, I have decided to speak this morning upon beryllium, and especially upon those peculiarities of the element which stand out prominently as characteristic of itself. I realise fully the narrowness of the subject, and fear that what I have to say will scarcely be of interest to all of you, but must plead as my excuse that, realising fully the limitations of my own knowledge, I can select no other subject with which I am more familiar.

Even at its christening beryllium started on a vagarious career, and its early sponsors, as well as those who followed, have recognised it under different names, and have ascribed to it and to its compounds properties as widely variant as the conditions under which they worked. Referred to first by Vauquelin, its discoverer, as "la terre du Béril," the German translators naturally adopted Berylerde as the name of its oxide, and although Vauquelin later accepted, under virtual protest, the suggestion made that glucine be used on account of the sweetish taste of the salts of the element, the name never secured adoption outside of France, and in the early literature was frequently written glycine. When later the element itself was separated by Wöhler he used the term beryllium for the first time, and a few weeks later glucinium appeared in the French press due to Bussy's almost simultaneous discovery. It is useless to go into the subsequent usage of the term, or why the "i" was dropped and glucinum used

* Address by the Chairman of the Section of Inorganic Chemistry at the Toronto Meeting of the American Chemical Society, June 28, 1907.

for a time in American practice. It is sufficient, I think, to say that by far the majority of chemists of the world prefer and use the name beryllium in their conversation and writings, and since neither priority nor usage can be shown for glucinium it should be dropped as rapidly as possible in the interests of uniformity. I especially believe this to be true, since there is no prospect of its ever replacing the more popular and, in my opinion, more justifiable beryllium.

Although the literature of inorganic chemistry is quite generally overburdened with compounds which have no actual existence, and which have obtained place and been assigned formulæ simply by the *analysis* of solid phases obtained under variable conditions, and without other attempt to prove their individuality, it is doubtful if there is any branch of the field that needs more careful revision than the chemistry of beryllium. Its literature is full of errors. Compound after compound has been claimed which has no actual individual existence, but whose place in literature and whose formula depends solely upon analysis of mixed crystals, residues of evaporation, or indefinite gummy precipitates without attempt to separate the individuals present. Formerly this could not always be done, but with the more recent and simple applications of the phase rule to these problems there is no excuse for similar errors which, unfortunately, still continue to creep into our journals.

The metal beryllium itself has been but little studied, and for the main part simply as a dark steel-grey powder obtained by the reduction of its chloride by sodium or potassium, or as small hexagonal plates obtained by the electrolysis of its double fluorides in a manner quite similar to the production of aluminium. Its melting-point, its solution tension, and many others of its important properties have never been determined, and many diverse statements are to be found in regard to it although the very careful researches of Lebeau can undoubtedly be fully relied upon so far as he went into the subject. It is recorded, for example, that it does and it does not combine directly with hydrogen, sulphur, selenium, and phosphorus; that it is and it is not reduced from its oxide by aluminium and magnesium; that it has been produced (even manufactured) by the electrolysis of its bromide, and that its bromide is not a conductor of electricity. In each case the negative is probably true. For many years its valency was, and for that matter still is, a matter of dispute. Even before it was seen that the only vacant place for beryllium in the periodic system was between lithium and boron there were strong arguments for both its divalency and its trivalency on account of its close resemblance to both zinc and aluminium in its action. When Mendeleeff finally pointed out its proper place in his table the controversy grew even more animated, and most of the researches on the element in the seventies and eighties had the establishment of the true valency as the main object. All the early determinations of the specific heat lead to the figure 13·6 as the atomic weight, and it was not until Nilson and Pettersson, after conquering unusual difficulties in a masterly research, finally determined the vapour density of the chloride and established its formula as $BeCl_2$ that real light was thrown on the question. Shortly afterwards, in 1886, Humpidge showed that beryllium was abnormal as to its specific heat, which increased regularly with the temperature at which determined, until between 400° and 500° it approached normal with a value of 6·2. A determination of the vapour density of the bromide, of the acetylacetonate, and of the basic acetate, all seemingly in agreement with the idea of the divalency of the element, would have seemed to have settled the matter, and probably has done so, but the controversy itself goes merrily on. Wyrouboff still argues in his articles for the trivalency, and Tanatar claims that the basic acetate can only be explained on the supposition that the element is in reality tetravalent.

Of the binary compounds of beryllium only the oxide, the carbides, and the halides have any real standing in literature, although the sulphide has been made by Lebeau. Of these the oxide is the only one that is stable in ordinary moist air, and even it shows decided variability in its hydroscopicity for reasons not yet determined. Ordinarily white, it is said to be blue by Levi-Malvano when made from his hexahydrated sulphate, although it is almost inconceivable that the difference of two molecules of water in the sulphate should cause this change. The halides, with the possible exception of the fluoride, can only exist in the complete absence of water, which cause them immediately and violently to lose part of their anion as hydracid. In this respect they are even more sensitive than the corresponding compounds of aluminium. On evaporating their solutions in water they lose more or less of the remainder of the gaseous hydracids, the residue becoming more and more basic, and remaining soluble until a surprising degree of basicity is reached. This hydrolytic action is comparatively small in the case of the fluoride, but is practically complete in the case of the chloride, bromide, and iodide. By careful manipulation residues of almost any degree of basicity, up to the pure oxide, can be obtained, and these mixtures of base and normal salt have given rise to claims for numerous *oxyfluorides* and oxychlorides for the existence of which there is no other evidence than the analysis of the variable residues obtained.

The hydroxide of beryllium is one of the most interesting of its compounds, and one that has properties which vary greatly with the conditions of its preparation. Among the most noteworthy may well be mentioned its great solubility, of from two to five equivalents, in concentrated solutions of its own salts, and its precipitation therefrom on dilution; its solubility in saturated solutions of acid sodium and ammonium carbonates, and its very much diminished susceptibility to reagents when dried at high temperature or boiled in water, as instanced by the fact that when freshly precipitated and washed with cold water, it will take up one-third of an equivalent of carbon dioxide, but on boiling becomes so immune to its action that the gas has been passed through it for three months without any considerable absorption.

Probably the fact which has the greatest bearing upon the chemistry of beryllium, and has caused more failures of researches undertaken upon the element than any other one thing, is the great influence which water has upon all of its salts, acting to many of them almost as if it were itself a strong hydroxide and in a manner that is hard to understand from our ordinary conceptions of solution and hydrolysis.

For this reason normal salts of the non-volatile acids only can be crystallised from water, and, indeed, but very few of them, such as the sulphate, the selenate, and the oxalate, have been so prepared. These are so strongly acid in reaction that they act almost as solutions of the acids themselves, attacking metals with evolution of hydrogen, setting free carbon dioxide from carbonates, and reddening litmus, even after surprising quantities of free base have been added. In spite of this fact the sulphate, chloride, and nitrate have been shown to be less hydrolysed, as determined by the sugar inversion method, than the corresponding salts of aluminium and iron, although they attack metals and carbonates vigorously even after many times enough excess of their own hydroxide has been dissolved to throw back the hydrolysis. Other normal salts like the nitrate can be prepared only by crystallising from concentrated acid, and even anhydrous acid yields only basic compounds in the case of the fatty acid series. Normal salts of more readily volatile acids, like the nitrite and carbonate, have not been produced at all, or only, as in the case of the sulphite, from absolute alcohol, or, as with the halides, by the direct combination of the elements themselves with special precautions to eliminate water. Many normal salts, such as the borates, the chlorates, the bromates, the iodates, the chromates, the acetates, &c., have not beeen obtained apparently because a concentration of acid sufficient to overcome the so-called hydrolytic solution tension of the salts cannot be attained.

On the other hand, only one *acid* salt, the mono-acid phosphate, has any real claim for recognition, and, although the peculiar nature of phosphoric acid would seem to render the existence of this compound as probable as any of an acid nature, its existence rests solely upon the testimony of a single analysis of a non-crystalline precipitate obtained by Scheffer nearly fifty years ago.

The action of water upon the compounds of beryllium is highly modified, as is the case with some of the compounds of aluminium and magnesium, by the entrance of another metallic element into the molecule, and some of the double salts of this element are well defined and readily obtained in the presence of water, where the simple normal salt could not be produced at all or only with difficulty. This is notably true of the double carbonates, chlorides, iodides, nitrites, and sulphites, although in general these salts have been studied but little, their discoverers being content with their identification and analysis. Among the double salts time permits of the mention only of the truly interesting double alkali tartrates and malates studied by Rosenheim and Itsig, and of the remarkable fact that the introduction of beryllium into their molecule enormously increases the molecular rotation of the compound, so that the diberyllium alkali tartrates have from five to six times the molecular rotation of the corresponding alkali bitartrates and the diberyllium malates a molecular rotation more than twenty times as great as the alkali bimalates. This is particularly surprising, since Walden has shown that beryllium has no undue influence upon the molecular rotation of the alpha brom-camphor sulphonates.

Some of the most interesting problems of the chemistry of beryllium lie in the equilibrium relations that exist between the various acid radicals and quantities of the oxide in excess of that required to produce the normal salt, *i.e.*, in the so-called basic compounds. It is certainly true that many of these acids can hold in solution phenomenally large amounts of beryllium oxide or hydroxide, extending in the case of the acetate to six equivalents, while the chloride can hold four, the sulphate three, and the oxalate nearly three equivalents. Even after these abnormal amounts have been dissolved the solutions still remain acid to litmus, and if heated in contact with basic beryllium carbonate the carbonate is attacked, the carbon dioxide set free, and an equivalent amount of hydroxide thrown out of solution. These highly concentrated solutions on being diluted with water throw down precipitates of a highly basic nature, or on evaporation leave gummy masses, the basicity of which depends upon the amount of the dissolved hydroxide, while physically they differ but little. Both the precipitated bodies and the residues of evaporation are amorphous and glassy in structure and vary widely in composition. The basic precipitates on equilibrium being reached approach closely to the hydroxide in composition, but always contain a small amount of occluded acid or normal salt which is impossible to entirely remove by washing. These facts have given rise in literature to a large number of so-called basic compounds which have no existence as independent individuals, but are in reality the impure hydroxide, or perhaps more properly come under the domain of homogeneous phases of variable composition or solid solutions.

It is, indeed, difficult to understand how the solution of the normal sulphate, nitrate, and chloride can dissolve several equivalents of their own hydroxide, attack metals and carbonates almost as vigorously as if they were the free acids themselves yielding these basic solutions, and still be less hydrolysed than the corresponding salts of aluminium and iron, as Leys and Brunner have both shown to be the case. It is, perhaps, equally difficult to demonstrate why the basic solutions so obtained should have less osmotic activity per equivalent of the acid present than the normal salts, should show no indication of a colloidal nature, and should contain no complex anion, but this is, indeed, the fact. The most probable explanation would seem to be that we have here a case of simple solution of a substance (beryllium hydroxide) in a mixed solvent (water and normal salt) in one of which alone (water) it is insoluble. The whole action of these solutions is perfectly analogous to those cases where a substance being dissolved in a mixed solvent *raises* the freezing-point whenever it is insoluble in that component which separates as the solid phase on cooling, and which Lach Miller has mathematically shown is a necessary sequence of the theorem of Gibbs.

In contradistinction to the basic solutions, solid or liquid, already mentioned, we have the truly phenomenal and actually basic compounds of beryllium, discovered in Urbain's laboratory by Lacombe, which are produced pure only in contact with anhydrous acid, or acid so nearly anhydrous that the mass of the water present becomes negligible to produce hydrolysis. These very interesting volatile and perfectly unique basic compounds are apparently confined to the fatty acid series, and have the general formula $Be_4O(AC)_6$. Of these the formate, acetate, propionate, butyrate, isobutyrate, and isovalerianate have been made and studied.

And now after this brief summary of the main characteristics of the chief classes of beryllium compounds I must, in closing, honour those who have been most prominent in developing our knowledge of this element by mentioning the names of Vauquelin, Wöhler, Bussy, Andejew, Weeren, Debray, Joy, Gibbs, Atterberg, Nilson and Pettersson, Humpidge, Hartley, Krüss and Moraht, Lebeau, Rosenheim and Itsig, and Urbain and Lacombe, and paying my sincere respect to the many others who, from time to time, have struggled through the difficulties incident to the peculiar and decidedly vagarious action of this element to greater light and truth. And, finally, I feel that I should call the attention of this Inorganic Section most particularly to the fact that not only the future chemistry of beryllium, but of all the elements in our branch of the greatest of sciences, is becoming more and more dependent for its exactness and wealth of discovery upon the application of those laws which are now correlated under the head of physical chemistry. At the same time we must not be engulfed by this more recent branch of our science, but must always look to her as the handmaiden and not the mistress.

A REVISION OF THE ATOMIC WEIGHT OF POTASSIUM.*

THE ANALYSIS OF POTASSIC CHLORIDE.

By THEODORE WM. RICHARDS and ARTHUR STAEHLER.

Introduction.

THE atomic weight of potassium is a chemical constant of unusual interest and significance. Standing as it does in the middle of the series of five atomic weights of the most electro-positive metals—substances which exhibit in a highly marked degree both similarity and progressive change in properties—this number must be of unusual importance in the search for that undiscovered mathematical relationship which undoubtedly exists between these constants. Moreover, the atomic weight of potassium is essentially bound up with the atomic weights of oxygen, chlorine, and silver, this group forming a fundamental basis in the calculation of nearly all the other atomic weights; so that a change in the atomic weight of potassium has a widely ramified effect on the whole table of atomic weights. If any further evidence of this fact were needed, the recent paper of R. W. Gray would furnish it (*Journ. Chem. Soc. Trans.*, 1906, lxxxix., 1175).

The recent investigation upon the atomic weight of sodium by one of us in conjunction with Dr. R. C. Wells (Richards and Wells, Carnegie Inst. of Washington *Publication* 28; *Journ. Am. Chem. Soc.*, 1905, xxvii., 459; *Zeit. Anorg. Chem.*, 1905, xlvii., 56) showed conclusively that Stas's work, upon which rested earlier knowledge,

* *Publication* No. 69, Carnegie Institution of Washington.

was somewhat at fault in several respects. The most serious of these errors were, first, the existence of impurity in Stas's silver; secondly, the fact that in his work solid salt was dropped into the argentic solution, causing occlusion of salt; and thirdly, inadequate knowledge concerning solutions of argentic chloride. In view of these errors it seemed not impossible that a similar revision of potassium might likewise yield slightly lower results for potassium than had been found by this master of exact analysis. For this reason the present investigation was undertaken.

Before describing the present work a brief historical review of previous investigations may not be out of place. The determinations may be divided into two groups—the first group including all of these determinations in which the molecular weight of a potassic halide was found by decomposition of a chlorate, bromate, or iodate, and the second group, those in which data for determination of the relation of potassium to chlorine, bromine, or iodine were obtained. The second group alone is concerned with the present work.

The early work of Berzelius, Pelouze, and Marignac need scarcely be considered here. (For a brief discussion of this work Clark's "Re-calculation of the Atomic Weights," 1897, p. 41, may be consulted). It dealt for the most part with the precipitation of argentic chloride from a solution of potassic chloride, and gave very widely discrepant results. Even the later work of Marignac on chloride, bromide, and iodide of silver was of doubtful value, especially the last; and accordingly until the present research was undertaken, the atomic weight of potassium rested chiefly on the analyses of potassic chloride made by Stas, by Richards and Archibald, and by Archibald alone, and upon the analysis of potassic bromide made by Stas.

As in the case of sodium, Stas made several series of determinations of the amount of silver needed to precipitate a known amount of potassic chloride (*Mém. Acad. Roy. Belg.*, 1880, xliii.; also "Œuvres Posthumes," edited by W. Spring; see Clarke's "Re-calculation," 1897, p. 42). One of these series was made in 1865, a later one in 1881, and yet another shortly before his death. The earlier series, although in some respects more careful and thorough than the later ones, was greatly at fault, because in it he overlooked the solubility of argentic chloride. Accordingly, of this work only the later need be considered. The mean of seventeen analyses indicated that 100 parts of silver were equivalent to 69·122 parts of potassic chloride, corresponding to an atomic weight for potassium of 39·130, if silver is taken as 107·93 and chlorine as 35·473. Later, Richards and Archibald (*Proc. Am. Acad.*, 1903, xxxviii., 443; *Zeit. Anorg. Chem.*, 1903, xxxiv., 353) found as a side issue of a research upon the atomic weight of cæsium that 100 parts of silver correspond to 69·115 parts of potassic chloride, and also that 100 parts of argentic chloride correspond to 52·002 parts of potassic chloride; and still more recently Archibald found results not very different (*Trans. Roy. Soc. Canada*, 1904, [2], x., III., 47). With the values given above for silver and chlorine these results indicate a value for potassium of 39·123 and 39·128 respectively, in the case of Richards and Archibald, and 39·122 and 39·135 respectively in Archibald's research.

In the case of the bromide Stas found in an unusually varying series of experiments that 100 parts of silver needed 110·346 parts of potassic bromide for complete precipitation, a result not very far from that of the less precise early work of Marignac. If Baxter's value for bromine (79·953) is accepted (*Journ. Am. Chem. Soc.*, 1906, xxviii., 1322), this corresponds to an atomic weight for potassium of 39·143, noticeably higher than the results from the chloride. At that time the discrepancy did not appear, because the atomic weight of chlorine was not properly evaluated, Stas believing that his work on the chloride also indicated an atomic weight above 39·14.

In view of the fact that these results differ among one another to an extent beyond a reasonable limit of experimental error, it seemed advisable to investigate once more the atomic weight of potassium in order to detect the cause of the discrepancy. This appeared to be especially desirable on account of the recent gain in knowledge concerning the peculiarities of argentic chloride in solution. Accordingly, the present research was begun, and simultaneously another concerning potassic bromide. A description of the latter investigation follows immediately after this one.

An investigation upon atomic weights naturally resolves itself into several different portions—first, the preparation of the pure material; second, the method of drying and weighing this material; third, the details of the analysis and the calculation of the results. These will be considered in order in the following pages. (A somewhat less detailed statement of this work has appeared in the *Berichte*, 1906, xxxix., 3611).

Preparation of the Material.

Potassic Chloride.— Several methods of preparing potassic chloride were tried, the most efficacious being adopted. The problem, of course, was to effect the elimination of other metals and other acids, especially those of the same groups. Both ends are most quickly and completely attained by incorporating into the process of preparation successive crystallisation of different salts, in order to eliminate by the crystallisation of one salt an isomorphous substance which might have been retained during the crystallisation of another salt. The commonest salts of potassium were therefore studied in relation to their fitness for the elimination of impurities in this way.

In the first place, on account of the good results which Richards and Wells have attained in preparing pure sodic chloride from re-crystallised sodic sulphate by precipitation with gaseous hydrochloric acid, sulphate of potassium also was early considered. This method was, however, soon abandoned, because the relative solubilities of potassic sulphate and chloride are far less favourable for the purpose than those of the sodium salts. The method of Archibald, who converted sulphate into chloride through precipitation with baric chloride, is complicated and involves the double work of preparing pure baric chloride as well as pure potassic sulphate. Moreover, it is not easy to eliminate the last trace of baric sulphate from the resulting salt. This also was rejected.

Next potassic chlorate was studied—a salt which had already been used by Stas for the preparation of pure potassium material. Both in crystalline form and in solubility this salt is very suitable for the separation of sodium from potassium material. Sodic chlorate crystallises in regular crystals which are six times as soluble in hot water and sixteen times as soluble in cold water as the monaclinic crystals of potassic chlorate. On the other hand, the data concerning the crystalline form and solubility of the chlorates of rubidium and cæsium are not sufficient to enable one to make any certain prediction with regard to their behaviour, and therefore experiments were made in order to discover whether or not these salts could easily be separated from potassic chlorate by re-crystallisation. The four salts of sodium, potassium, rubidium, and cæsium were mixed together and qualitatively separated by fractional crystallisation. The sodium was effectively separated from the crystals; but after three careful crystallisations the cæsium line, although stronger in the mother-liquor than at first, was still not absent from the crystals. Indeed, neither rubidium nor cæsium lines had considerably diminished therein. Accordingly, this method was also abandoned.

Potassic nitrate showed itself to be much more satisfactory in its behaviour. Its usefulness did not seem at first so certain as to be a foregone conclusion, especially as Stas had not succeeded in preparing a particularly pure material from this salt. Probably this failure was due to the circumstance that he carried out the crystallisation in glass vessels, which of course continually introduced sodium and silica. The rather inadequate data concerning the four nitrates may be well put together as follows:—

Solubility in 100 Parts of Water.

	Cold.		Warmer.		
	Temperature.	Parts.	Temperature.	Parts.	Crystalline form.
$CsNO_3$.	3°	12	60°	Very many	Tetragonal
$RbNO_3$	0°	20	10°	43	Needles
KNO_3..	14°	25	114°	337	Rhombohedral and rhombic
$NaNO_3$	15°	84	114°	200	Rhombohedral

Because this series of results is not entirely conclusive, although promising, a series of crystallisations was carried out here also. This series showed that an admixture of the three other nitrates with a large excess of potassic nitrate was nearly all eliminated by as few as two crystallisations. The separation of the sodium was especially marked in the spectroscopic tests. This method therefore appeared very well suited for the preparation of pure potassium material, which might easily be converted into chloride after the other metals had been eliminated.

Pure potassic nitrate of commerce, obtained from Germany, was dissolved in a little water, freed from solid substances by filtration, and crystallised twice in Jena glass flasks. The salt was each time freed from the mother-liquor in a porcelain centrifuge (Richards, *Journ. Am. Chem. Soc.*, 1905, xxvii., 105). The resulting material was four times subsequently re-crystallised in platinum vessels, and whirled in a platinum centrifuge. The pure crystals were now divided into two parts; one part was dried in a vacuum desiccator, while the other part was subjected to yet six more crystallisations and whirlings in platinum vessels.

It now became a question how this nitrate could best be converted into chloride. The method recommended by Stas of heating the salt with pure ammonium chloride involves not only the preparation of this latter salt in a pure state, but also great danger of contamination from the vessel, whether of platinum or porcelain. Platinum is especially attacked because of the action of the oxychlorides of nitrogen and of chlorine. The more favourable method appeared to be to convert the nitrate into chloride by repeated evaporation with hydrochloric acid in quartz dishes. This method was found to have two objections. In the first place, dishes large enough for the raw material were not to be had. Moreover, the tendency of the branching crystals to grow over the edge of the dish caused serious loss of material and danger of impurity. Neither could potassic nitrate be heated to a high temperature with ammonic chloride, or in the steam of hydrochloric acid in quartz dishes; for there is always danger that the reaction $4KNO_3+2SiO_2=2K_2SiO_3+4NO_2+O_2$ would occur (Richards and Archibald, *loc. cit.*).

Because Stas had never been able to obtain a salt free from silica when working in glass vessels, we desired to avoid completely the use of glass. Therefore, only one way remained, namely, to convert the potassic nitrate into chloride by precipitation with hydrochloric acid in a platinum dish. The resulting aqua regia must naturally attack the platinum, but we preferred this impurity to that of silica, and found, moreover, that the amount of platinum dissolved is very small. In the presence of large masses of potassic salts, aqua regia, especially in the cold, dissolves platinum but little. For example, in one experiment in which about half a kilogrm. of potassic nitrate was treated with hydrochloric acid gas, only three-tenths of a grm. of platinum was converted into the form of potassic chlorplatinate. In subsequent crystallisations the amount was very much less, because the great mass of the nitric acid was eliminated by the first crystallisation. After the third re-crystallisation, the diphenylamin reaction failed to reveal the presence of any retained nitrate.

The precipitation was carried out in the following manner:—The often re-crystallised, very pure potassic nitrate was dissolved in the least possible quantity of cold water, contained in a platinium dish, packed in ice. Slowly, in order to prevent warming, hydrochloric acid gas was run into this solution. The gas was supplied by warming a pure concentrated solution, and was passed into the nitrate solution through an inverted platinum funnel. The potassic chloride, which appeared somewhat yellow from its slight platinic impurity, was whirled in the platinum centrifuge and dissolved in purest water. Potassic chlorplatinate is practically insoluble in a concentrated solution of the chloride, as the law of concentration effect and the theory of ionisation predicts; hence the impurity was easily separated upon a small pure filter. The clear colourless solution was again saturated with hydrochloric acid, and the same round of operations repeated. Upon a third repetition of this process, the nitric acid was eliminated, and the salt, as a rule, was wholly colourless in consequence. On no occasion, even with large amounts of materials, did perceptible colour remain after five treatments. No specimen was subjected to less than seven such re-crystallisations, while some were passed yet five times more through the precipitation and centrifugal drying. Assuming that each time about three quarters of the ordinary adhering mother-liquor was removed by the centrifugal separation, these crystals must have been as free from heteromorphous substances as if they had been re-crystallised many thousand times in the ordinary fashion. It will be shown that all the samples gave the same results upon analysis, hence further purification according to this method was needless. The salt was found to be wholly free from sodium by a sensitive spectroscopic test. It was in every case freed from acid by a single re-crystallisation from the purest water and by fusion in the manner to be described later.

Seven different samples were prepared after this fashion from varying raw material. These are given in the list below.

a. The pure potassic material ("C.P." of German preparation) was re-crystallised as nitrate six times, and precipitated as chloride seven times. This salt after the final re-crystallisation from pure water was dried in a platinum dish at 120° in an electric oven. The salt was snow-white, and was as clear as water when fused, as, indeed, were all the other samples.

b. This sample was similar to *a*, but obtained by the evaporation of the final aqueous mother-liquor decanted from *a*. The mother-liquor from *b* was rejected.

c. Five extra precipitations with hydrochloric gas (or twelve in all) yielded this salt, which was prepared for analysis in the same way as *a*.

d. This salt bore the same relation to *c* that *b* bore to *a*, being essentially identical with *c*.

e. For this sample and the next one the nitrate was re-crystallised twelve times, and the chloride precipitated seven times.

f. From the final mother-liquor of *e*, *f* was prepared, as *b* followed after *a*.

x. This sample was exactly like *a*, except that the raw material came from an entirely different source.

Argentic Nitrate.—The nitrate of silver used for precipitating chlorine in the analysis was crystallised three times from pure dilute nitric acid solution, and each time centrifugally freed from mother-liquor. Before each analysis the aqueous solution of the salt was tested in the nephelometer for a possible trace of argentic chloride, and no material was ever used which showed to this exceedingly sensitive test the least trace of impurity (see Richards, *Proc. Am. Acad.*, 1894, xxx., 385; *Zeit. Anorg. Chem.*, 1895, viii., 269). For preservation in a pure state it was kept in a tight desiccator over potash.

Silver.—The metallic silver used in the research was made from argentic nitrate which had been six times re-crystallised. The metal was precipitated as fine powder by ammonic formate (Richards and Wells, *Journ. Am. Chem. Soc.*, 1905, xxvii., 475), melted on pure lime, and further purified by electrolysis (J. L. Hoskyns Abrahall, *Journ. Chem Soc. Trans.*, 1892, 660; also Richards, *Proc. Am. Acad.*, 1893, xxviii., 22). The beautiful crystals thus

prepared were fused in a stream of pure electrolytic hydrogen, and finally in a vacuum of 0·1 mm. The metal was supported on a boat of the purest lime, prepared from calcic carbonate precipitated from the nitrate for this purpose. The boat was provided with several compartments, each of which held enough silver for one analysis, in order to avoid the possible introduction of impurity into the metal by subsequent cutting. It was enclosed in a stout porcelain tube, provided with Hempel water-cooled stoppers, and was heated electrically in a Heraeus tube-furnace (Heraeus, *Zeit. f. Elektrochemie*, 1902, viii., 201). The vacuum was maintained by a motor-driven Geryk oil air-pump. Except for these minor improvements, the preparation was essentially similar to the best methods employed by Richard and Wells in their often-cited work, to which the reader is referred for further details.

Nitric and Hydrochloric Acids.—Very carefully tested preparations of commerce were used as the raw materials in the preparation of these acids. They were re-distilled with platinum condensers until they were fully pure enough for the purposes for which they were needed. The hydrochloric acid had been shown in the research on sodium to be free from bromine or iodine.

Water.—This substance, because it is used in larger quantities than any other, must be especially pure. All the water used, either for preparation or analysis, was twice distilled, once with alkaline permanganate and once alone. For the best work a platinum condenser was used. All that was needed for analysis was tested in the nephelometer immediately before use.

(To be continued).

CORRESPONDENCE.

RELATION BETWEEN VALENCY AND ENERGY.

To the Editor of the Chemical News.

Sir,—In reply to Mr. le Bas's letter on the above subject (Chemical News, xcvi., 58), I would beg you to insert the following:—

Mr. le Bas states that I assume that the C.H and C.C links have different values; he regards them as having equal values, namely, zero; which seems to be tantamount to denying their existence.

A priori we must regard every link as being equivalent to so much energy, and naturally until proof is offered to the contrary we must regard different links as corresponding to different amounts of energy; thus my treatment of the question involves no assumption.

If we may assume that the C.C and C.H links have equal values, then we may with equal truth assume any and all links as equal, from which it would follow that most chemical changes would be unaccompanied by heat changes, which is contrary to fact. This shows the assumption to be untenable.

Mr. le Bas's letter contains the extraordinary statements that the heat of combustion of an isolated carbon atom is represented by $C+4\frac{L_1}{2}$, and that of an isolated hydrogen atom by $H+\frac{L_1}{2}$. It is apparent that he is using my constants with a different meaning from that which I applied to them.

I would beg to suggest a perusal of the opening paragraphs of my article in the Chemical News (xcv., 301), also the definitions given in the former article (Chemical News, xcv., 193).

The heat of combustion of an isolated carbon atom is the algebraic sum of the heats due to the severance of one O=O link, and the formation of one molecule CO_2 from its constituent atoms, dealing with a grm. atomic weight of carbon; it is by definition equal to C cals.

The heat represented by the expression $C+4\frac{L_1}{2}$ cals. is, however, the algebraic sum of the above and the heat due to the severance of 2 C.C links; Mr. le Bas therefore assumes that no heat is either absorbed or evolved when this link is severed, *i.e.*, $L_1=0$; which apparently he is attempting to prove. Similarly for hydrogen.

The use of the symbols :C: and H. for isolated carbon and hydrogen atoms respectively in this connection, is misleading, for I have already employed them to stand for combined atoms (*i.e.*, :C: stands for a carbon atom plus four links of some sort, and H. for a hydrogen atom plus one link), as was apparent from the context. Thus, I stated that :C: had different values in CH_4, C_2H_6, &c., not because the value of the carbon atom itself was altered, but because it was linked differently.

Examining Mr. le Bas's "proof" that $L_1=L=0$, we find him arguing in a circle; I have pointed out one occasion on which he assumes this equation; moreover, the assumption $L_1=0$ is made in calculating the values of C and H, for he states:—

$$2H = \text{M.H.C. } CH_4 - [CH_2] = 210{\cdot}8 - 158{\cdot}2 = 52{\cdot}6;$$

whereas, making no assumption, it should be (using Mr. le Bas's figures):—

$$2H - L_1 = C + 4H - [C + 2H + L_1] = 210{\cdot}8 - 158{\cdot}2 - 52{\cdot}6,$$

whence $H - \frac{L_1}{2} = 26{\cdot}3$.

Thus, all that is proved that $H - \frac{L_1}{2} = H - \frac{L_1}{2}$, which was self-evident before! (see Note).

(Note.—I consistently use the symbol H to stand for the value of one hydrogen atom plus the value of one C—H link).

With regard to Mr. le Bas's hypothesis, he admits that it is inadmissable to apply the relation $c = \frac{\text{M.H.C.}}{W}$ to unsaturated compounds, *i.e.*, he admits that M.H.C. is not equal to W.*c.* in these cases; this is what I wanted my figures to point out.

Mr. le Bas now proposes the following formulæ:—

For olefins, $\text{M.H.C. } C_nH_{2n} = |\ = 6n\,c + |\ = |\ ;$ and for acetylenes, $\text{M.H.C. } C_nH_{2n-2} \equiv |\ = 6n\,c - 2c + |\equiv|$, where $|\ = |$ and $|\equiv|$ are constants; but these equations are in direct contradiction to the statement made by Mr. le Bas (*Proc. Chem. Soc.*, xxiii., 134), that the molecular heats of combustion of the hydrocarbons are proportional to their valency numbers W, and I take it to be a tacit admission that this statement is incorrect.

The question of trimethylene I have dealt with at some length (Chemical News, xcv., 302).

The value $c=26{\cdot}25$ is calculated thus:—According to Mr. le Bas's hypothesis c is the heat equivalent of one hydrogen atom expressed in large calories; moreover, according to him the value of the C.H and C.C links are negligibly small so that—

$$c = \tfrac{1}{4}(2H - L_1) = \tfrac{1}{4}\beta = 26{\cdot}25.$$

The correctness of my values for the "fundamental constants" (a, β, γ, δ) is proved by the *very small* differences between the experimental and my calculated results.

Mr. le Bas stated in his note in the *Proc. Chem. Soc.* that the heat of combustion of a substance may be regarded as made up of (a) an absorption of heat due to the dissociation or decomposition, and (b) an evolution of heat due to the combination of the isolated atoms with oxygen; he further stated that the factor (a) is negligibly small compared with (b). This latter statement is an assumption, and I have pointed out that it is incorrect because two at least (though not necessarily the C=C and C≡C, and possibly all three) of the various carbon links have large values, as is apparent from the values of the expressions $L_2 - 2L_1$ and $L_3 - 3L_1$.

Mr. le Bas does not refer to my criticism regarding the use of uncorrected M.H.C.'s.

It is not suggested that Mr. le Bas's hypothesis (rightly stated) is valueless, for the general equation, of which only particular cases have been noted, can be deduced by means of my own constants, the validity of which I have demonstrated; thus, in the general expression for a hydrocarbon put $L_2 = 2L_1 + T_2$, $L_3 = 3L_1 + T_3$, and also add T for any other tension (see CHEMICAL NEWS, xcv., 301); then we obtain—

$$nC + 2(n + 1 - a - 2b - p)H + (n + p + a + 2b - 1)L_1 + aT_2 + bT_3 + T = na - (n + p + a + 2b - 1)\beta + aT_2 + bT_3 + T,$$

but *approximately* $4\beta = a$; therefore the above expression—

$$= (3n + 1 - a - 2b - p)\beta + aT_2 + bT_3 + T$$
$$= \{4n + 2(n + 1 - a - 2b - p)\}k + aT_2 + bT_3 + T, \text{ if } k = \tfrac{1}{4}\beta.$$
$$= W.k + aT_2 + bT_3 + T, \text{ which is the general expression.}$$

It must be, however, carefully noticed that this should be only regarded as a "working rule," and not as a law from which we should be likely to obtain any knowledge of valency, for the following reasons:—1. It depends entirely on the accidental relation $4\beta = a$, and thus does not hold for compounds other than hydrocarbons in general. 2. It is approximate only—not accurate—as I have shown; the error introduced by saying $4\beta = a$ becoming noticeably large for hydrocarbons of high molecular weight. It should also be noticed that k is not defined as the thermal equivalent of an isolated hydrogen atom.—I am, &c.,

H. STANLEY REDGROVE.

The Polytechnic, Regent Street, W.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

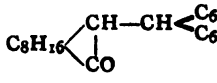
Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlv., No. 5, July 29, 1907.

Ortho- and Pyroarsenic Acids.—E. Baud.—The hydrate, $As_2O_5.4H_2O$, is deposited in a crystalline state in the cold from a concentrated solution of arsenic acid, and when it is heated to 110° $2As_2O_5.3H_2O$ is obtained. The former, when kept over sulphuric acid for several days under a clock-glass, remains unaltered provided that the temperature does not exceed 10°, but above this temperature, *i.e.*, at about 15° or 20°, the crystals effloresce, and lose exactly $2H_2O$. The product is $As_2O_5.2H_2O$, or pyroarsenic acid. Orthoarsenic acid can exist only in solution. When its solution crystallises it leaves the hydrate of pyroarsenic acid, which effloresces at about 15°, and gives pyroarsenic acid. From the thermic point of view the latter is closely analogous to pyrophosphoric acid.

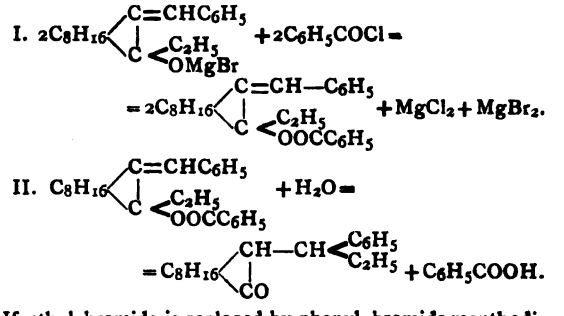
Direct Oxidation of Phosphorus.—E. Jungfleisch.—The products of the direct and spontaneous oxidation of phosphorus at a low pressure are not the same as those formed when the pressure is high. In pure oxygen at atmospheric pressure the oxidation of pure dry phosphorus in the cold gives exclusively phosphoric anhydride; in the same gas at a pressure of 18 to 20 mm. the products of oxidation are phosphorous anhydride, P_2O_3, and a bright yellow compound, which, when dissolved in alcoholic potash and precipitated by hydrochloric acid, gives the suboxide, P_4O. The process of oxidation is accompanied by characteristic phenomena, the P_2O_3 bursting into flame spontaneously. Whenever oxygen acts at a low pressure upon phosphorus, whether the pure gas, air, or a mixture of oxygen and an inert gas is used, the results obtained are always the same. In presence of water the substances produced by its action on the same compounds are obtained, and this oxidation of phosphorus at low pressures may render it spontaneously inflammable in air in the cold. For instance, if pieces of pure dry phosphorus are placed in a tube closed at both ends by rubber corks, and the tube is filled with carbon dioxide and left in air, after some time the phosphorus near tbe corks begins to tarnish on the surface, while further from the ends of the tube it remains unchanged. The oxygen of the air diffuses through the corks, and slowly reaches the phosphorus, covering it with P_2O_3 and the yellow compound. Then the pieces of phosphorus near the ends catch fire owing to the spontaneous combustion of the P_2O_3. The phosphorus which has not been reached by the oxygen remains unchanged, and does not catch fire. The same transformation into spontaneously inflammable phosphorus is effected much more rapidly if the apparatus is closed by a thick rubber tube, through the walls of which the diffusion of oxygen takes place more quickly. Phosphorus also becomes spontaneously inflammable when P_2O_3 is formed even in very small quantities on its surface, under various circumstances which the author has investigated.

Properties and Constitution of Tantalum Steels.—Léon Guillet.—The author has examined the micrography and mechanical properties of normal and tempered tantalum steels containing different percentages of tantalum, and finds that very small quantities of the element have a more marked effect upon tempered than annealed steels, the influence being independent of the amount of tantalum present. On the whole, the author finds that tantalum steels, at any rate when they contain but little carbon, have no special properties to recommend them, although it has frequently been stated that the addition of tantalum considerably improves steels.

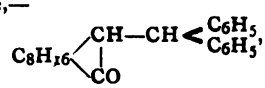
Derivatives of Menthone.—Eyvind Bœdtker.—Organomagnesium compounds do not act upon ethyl menthone, but an energetic reaction occurs with benzylidene menthone, the product being menthoethylphenyl methane,—



The reaction probably takes place in two stages:—



If ethyl bromide is replaced by phenyl bromide menthodiphenylmethane,—



is obtained. When benzoylchloride is added to the mixture of benzylidene menthone and magnesium phenyl bromide, stereoisomers are produced, two of which the author has isolated by fractional crystallisation in alcohol. The author has also prepared menthomethyl-, normal propyl-, isobutyl-, and isoamyl-phenylmethane, but as yet he has obtained them only in the form of syrups, which are shown by analysis to be impure.

Two New Glucosides, Linarine and Pectolinarine.—T. Klobb.—In the flowers and leaves of *Linaria vulgaris* two glucosides occur; one of these substances, which has been called linaric acid, has been shown by the author, in collaboration with M. Fandre, to be insoluble in ammonia and also in alkaline carbonates, and it is therefore not an acid; they proposed the name linarine for it. When

oxidised it yields a volatile substance, $C_9H_{10}O_2$, and it behaves like a very stable glucoside, which is not hydrolysed by weak acids at the temperature of the water-bath, but is split up by 10 per cent hydrochloric acid at 100—110°, and by concentrated hydrochloric acid in the cold. The second substance, pectolinarine, is also a glucoside, but it easily splits up with weak acids. It differs from linarine by its additional water of constitution. Both glucosides give on hydrolysis a sugar and a mixture of crystalline substances, linaric phenol and anhydrolinaric phenol. By the action of alkalis pectolinarine is transformed into a β-modification, which on hydrolysis gives only linaric phenol, and linarine under the same conditions gives a β-modification, which when hydrolysed gives only anhydrolinaric phenol. Pectolinarine is nearly insoluble in cold water, but dissolves in boiling water and in alcohol, giving solutions which, when saturated, gelatinise on cooling. It is very soluble in concentrated hydrochloric acid and in caustic potash, and when boiled for a long time with water it is transformed into crystalline linarine, losing water of constitution. The formula of linarine appears to be $C_{50}H_{50}O_{25}$, and if the sugar formed is a hexose the hydrolysis can be represented provisionally by the equation—

$$C_{50}H_{50}O_{25} = \underset{\text{Linaric phenol.}}{C_{19}H_{14}O_7} + \underset{\text{Anhydrolinaric phenol.}}{C_{19}H_{12}O_6} + 2(C_6H_{12}O_6).$$

No. 6, August 5, 1907.

Platinum Silicide and a New Double Silicide of Platinum and Copper.—Em. Vigouroux.—Platinum silicide of formula PtSi is formed by the direct union of the elements provided that excess of silicon is present. When this silicide is heated with aluminium it tends to decompose, while copper gives a residue containing traces of silicon and 99 per cent of platinum. The copper silicide, $SiCu_4$, appears to act as a reagent effecting combination, either with this platinum silicide or with free platinum, giving in the latter case a compound of formula $SiCu_2Pt$.

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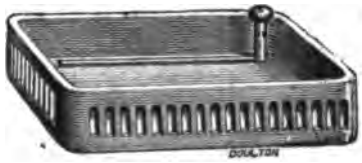

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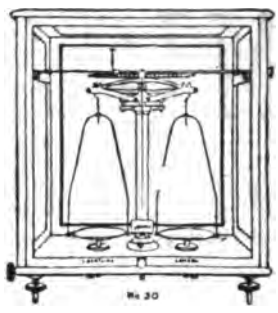

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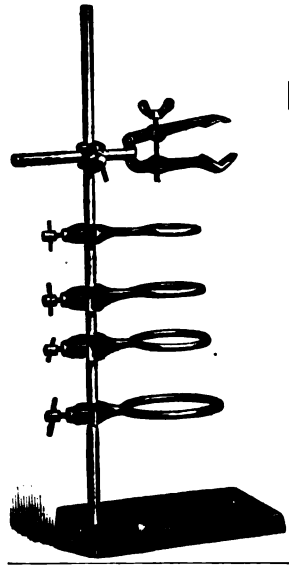

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THE CHEMICAL NEWS.

Vol. XCVI., No. 2495.

DIMINUTION IN LENGTH OF COTTON AND LINEN FIBRES DURING THE PREPARATION OF "STUFF" FOR THE MANUFACTURE OF PAPER.

By CLAYTON BEADLE and HENRY P. STEVENS.

As very little work has been done in the direction of measuring the actual length of the fibres during the process of beating in the preparation of pulp for the manufacture of paper, the authors made arrangements with a well-known firm of paper-makers to withdraw samples of pulp from the hollanders, of the ordinary type and of about 3-cwt. capacity, during the beating operation, and whilst the beaterman manipulated the roll in the ordinary way for the manufacture of the paper that he had to provide for. In this manner, in the work about to be described, samples of pulp were taken every hour. There was no attempt to determine the length of the fibre at the commencement of the beating, as when the fibres are in the condition of rag "half-stuff" it is almost impossible to arrive at even an approximate estimate by means of measurements under the microscope. It might be assumed, however, that the cotton and linen fibres as "half-stuff" are intact, and therefore an average length of each, based on published figures, may be taken as representing the length of the fibres as half-stuff. As, however, such a figure is a pure assumption, the length of fibre is given in tables and curves as from the end of the first hour in each case. Furthermore, measurements made at an earlier stage in the beating would have no practical value.

With very long stuff, or stuff that has been very little beaten, it is extremely difficult to arrive at the average length, because it requires a great deal of experience to obtain on the "field" a representative set of fibres, many of them being in the form of threads or small woven particles. When, however, the work of unravelling the threads is accomplished the measurement can be more easily made. Where possible, two sets of readings were taken of each sample, each set consisting of ten determinations for length and diameter. The measurements were made under a magnification of seventy-two diameters. The average of each set should bear a fairly close correspondence with one another, and each set should be the result of measurements of different "fields." As indicating the extent to which the individual fibres varied in length, we give in Table I. details of measurements for the ninth hour. In Table II. we give a summary of this trial on linens beaten for ten hours. Tables III. and IV. are summaries of similar trials.

It will be noticed that, in the case of Table II., there is, with one or two exceptions, a decrease in length of the fibre from hour to hour. The same will be noticed in respect to Tables III. and IV. Where the fibres showed any marked irregularities, the work was carefully repeated, and it was finally found that, in the case of the linens, a diminution in length could be represented by Curves A and B.

In the case of the cottons (Curve C) the diminution is apparently somewhat spasmodic, the result possibly of a

Table I.—*Details of Measurements of Linens after Nine Hours' Beating.*

Length. Mm.	Length. Mm.
2·92	1·87
2·64	3·82
2·43	2·22
2·50	1·74
2·16	2·92
2·71	2·82
2·85	2·78
1·81	2·78
3·61	3·61
3·82	3·40
Mean .. 2·74	2·80

Mean length of twenty readings .. .. 2·77 mm.
Mean diameter of first ten readings .. = 0·0187
" " second ten readings = 0·0181
" " twenty readings .. = 0·0184

Table II.—*Examination of Linen Pulp at different stages of the Beating for Length of Fibre.* (See Curve A).

(Beaten for 30 lbs. 21" × 33").

Hours of beating.	Average length. Mm.	Average diameter. Mm.
1	13·3	0·0222
2	9·4	0·0227
3	5·62	0·0260
4	4·37	0·025
5	3·92	0·023
6	3·37	0·021
7	3·58	0·020
8	2·89	0·0185
9	2·77	0·0184
(a) 10	2·14	0·023

(a) Taken on fibres from finished paper.

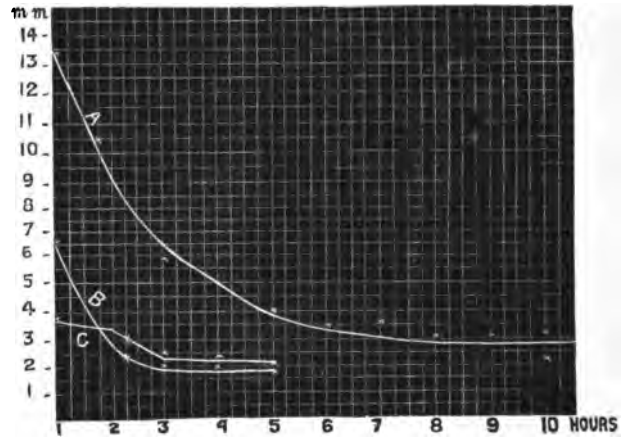
Table III.—*Linens Beaten for Five Hours at different stages of the Beating.* (See Curve B).

Hours of beating.	Average length. Mm.	Average diameter. Mm.
1	6·34	0·0177
2	2·84	0·0190
3	1·82	0·0186
4	1·94	0·0174
5	1·70	0·0199

Table IV.—*Cotton ("Scotch Fines") at different stages of the Beating.* (See Curve C).

(Beaten for 100 lbs. Imperial).

Hours of beating.	Average length. Mm.	Average diameter. Mm.
1	3·59	0·0185
2	3·40	0·0180
3	2·34	0·0208
4	2·26	0·0184
5	2·02	0·0181



Curves showing the Diminution in Length of Cotton and Linen Fibres during the Process of Beating from Rags.

sudden lowering of the beating roll. It will be noticed that, in the Curves A and B, during the first two hours there is a very great diminution in length, but during the second half of the beating the length is only influenced to a comparativly small extent. No doubt had we been able to take the actual length of the fibres before the beating commenced, we should have found possibly as much diminution during the first hour's beating as was to be noted in the other nine hours. Such curves have, as far as we are aware, never before been constructed.

The authors wish to express their thanks to their pupil, Mr. G. W. Ross, for his assistance in connection with the measurements.

THE ORIGIN AND OCCURRENCES OF THE DIAMOND.*

By Professor T. W. E. DAVID, F.R.S.

During the session of the British Association for the Advancement of Science at York in 1906, an interesting discussion was started on the above subject in connection with the exhibition of a diamond in the original matrix by Professor David. This specimen was discovered by Mr. A. R. Pike, of Oakley Creek, Copeton, near Inverell. Mr. E. F. Pittman, Assoc.R.S.M., Under Secretary for Mines and Government Geologist, has already recorded this occurrence and described the locality referred to in the annual report of the Department of Mines, N.S.W., 1904. He has also recorded the occurrence of diamonds in matrix at the Ruby Hill mine, on the road from Bingara to Tamworth. It may be mentioned that at the latter locality the rock considered to be the probable matrix of the diamond is of a mixed character. Portion of the hill is formed of agglomerate or volcanic breccia, covered by loose boulders of basalt. This agglomerate is traversed by dykes of basalt, and contains garnets and inclusions of a rock called eclogite. The eclogite rock is a rather coarsely crystalline mixture of garnet, lime, felspar, and the mineral known as diopside.

The diamonds which have been found in this locality are considered by Mr. Pittman to have been derived either from the volcanic breccia or from the basalt dykes which intersect it. Up to the present no undoubted specimen of this volcanic rock with a diamond actually in matrix in it has yet been found. The discoverers, however, Messrs. Pasley, Gordon, and Morkel, maintain that ten diamonds have been obtained by them at this mine from volcanic breccia taken out of their shaft and washed in a tub with a hand sieve. These ten diamonds are stated by Mr. Pittman to have weighed in the aggregate 4¼ carats. He adds that the diamonds were remarkable in that they each had a distinct depression of pitting on one of the faces. As will be recorded presently, similar phenomena may be noticed in the case of the diamonds more recently discovered in matrix at Oakey Creek. The latter discovery was the result of a theory held by Mr. A. R. Pike (of Messrs. Pike and O'Donnell) that the Copeton diamonds must have originated in certain local dykes or pipes. This view he has entertained for years, and after much patient work his researches were rewarded by the discovery of a diamond actually *in situ* in a lump of basis rock taken out of a tunnel which was driven through a 26 ft. thick pipe of dyke. This beautiful specimen of diamond in matrix shows it to be about two-thirds embedded amongst the crystalline minerals of the igneous rock. At a meeting of the British Association at York, England, as well as at the International Geological Congress of Mexico last September, this specimen was most critically examined by the chief scientific authorities on diamonds in the world, and all were satisfied as to the absolute genuineness of the discovery, and considered it of the highest possible scientific interest.

With a view of throwing light upon the nature of the rock forming the matrix of the diamond, a couple of thin slices were cut off from a corner of the diamond-bearing matrix. These were rubbed down by a lapidary until they were sufficiently thin for their constituent minerals to be recognised. It was then clearly demonstrated when the thin slices of the rock were placed under a microscope that the rock was quite unlike any which has hitherto been proved to form a matrix of the diamond in any other part of the world. This fact of course lends additional interest to Mr. Pike's discovery at Oakey Creek.

In addition to the remarkable specimen above referred to, a second diamond was exhibited by Professor David, both at York and Mexico, coming from the same mine. This diamond is about the same size as the first, and was picked up from off a heap of igneous rock at grass at the mouth of the tunnel at Oakey Creek. It was shed from a disintegrated fragment of the dolerite in the process of its becoming decomposed under the action of the weather. There can be no doubt from the statements of the finders that this diamond was not of alluvial origin, but was actually shed from the matrix itself. Moreover, even apart from the actual record of how it was found, the diamond bears internal evidence of having been derived direct from the original rock matrix. Professor Bonney, at York, called special attention to the interesting fact that the surface of this diamond was deeply pitted, and that portions of the original diabase matrix were embedded in the small pits. A careful microscopic examination of them showed that these little inherent fragments of matrix corresponded exactly in their contained minerals, &c., with the general character of the rock forming the matrix of the specimen first described. Messrs. Pike and O'Donnell treated about two loads of partly decomposed igneous rock from the same tunnel on their mine, and hand-sieved it; and although by far the greater part of the material so treated was thrown back in the form of lumps into the heap from which it was originally taken, two diamonds were obtained from it. The material treated in this primitive way weighed about 2 tons. Although about 45 tons of igneous rock have been mined, this has been stacked; and it is the intention of the syndicate to whom the mine now belongs to put this decomposed material, now in the form of rock lumps, through a rotary puddling plant such as is used in Africa. Water is, of course, needed for the purpose, and the syndicate are waiting until the present work they have in hand will give them the necessary supplies. The delay in further testing this 45 tons of igneous rock for diamonds has been entirely due to want of water. Until such tests are carried out it would be premature to hazard an opinion as to whether or not the mine where this very interesting discovery has been made is likely to prove remunerative.

The exhibition, particularly at York, of the two specimens of diamond above referred to and the discussions which ensued created the greatest possible interest amongst the assembled scientists. In the first place, with regard to the rock which forms the matrix of the diamond at Oakey Creek, this was examined both in the hand specimen as well as in the form of thin microscopic slides. A very complete chemical analysis of the rock was submitted both at York and Mexico. This had been prepared by Mr. Mingaye, analyst and assayer to the Geological Survey Branch of the Department of Mines, Sydney. The result of the microscopic examination, taken in conjunction with the nature of the analysis submitted, led them to class the rock as belonging to the variety known as hornblende-diabase. In no other part of the world has a diamond ever been found in a rock matrix like this. Hitherto the occurrence of diamonds in matrix, until this recent discovery by Mr. A. R. Pike, was restricted to the following kinds of rock:—

1. *The Diamond-bearing Volcanic Pipes of South Africa.*—These have the shape of roughly circular pipes, often

* From the *Mining Journal*, August 24, 1907.

several hundreds of yards in diameter. They appear to have formed the chimneys or explosion hollows connected with some violent deep-seated volcanic action. The rock which now fills them, and which therefore holds the diamonds, is of a fragmentary character of the nature of a breccia or agglomerate. The enclosed fragments are chiefly of igneous origin. and are formed mostly of dark and heavy eruptive rocks, some of which are allied to serpentine. It is interesting to note that in this breccia there are numerous fragments of a garnet-bearing rock. eclogite, very similar, as Mr. Pittman has pointed out, to the rock of the same name discovered at Ruby Hill, in New South Wales.

2. *Occurrence in Gneiss in Brasil.*—The only other occurrence of diamond in matrix in a terrestrial rock is perhaps that of a diamond in a specimen of gneiss found in Brazil.

3. *Meteoric Occurrence.*—The third form of occurrence is extra-terrestrial, and may be described as meteoric. Diamonds have been discovered in the nickel-iron meteorite of Canyon Diablo, in the south-west of the United States, not far from the Grand Canyon. Diamonds have also been discovered in the stony meteorite from Novo Urie, in Russia. It may be mentioned that some very curious hollow cubes of carbon in the form of graphite, discovered in the meteorites at Youndigin, in Western Australia, and provisionally classed as the mineral cliftonite, are now generally looked upon as pseudomorphs, after diamond—that is, cubes of carbon, which, while they retain the original physical constitution of that gem, becoming black and opaque, are very soft; in fact, in general physical character and composition closely resembling the carbon of a black-lead pencil. If this view as to their origin is correct the diamonds of the Youndigin meteorites were of much more than mere microscopic size.

The question may next be considered—Is there any possible light on the genesis of the diamond to be derived from its artificial manufacture? Amongst very numerous experiments on the subject the following three may be specially selected:—

Following up the clue given by the occurrence of microscopic diamonds in the Canyon Diablo meteorite, the distinguished chemist and mineralogist, H. Moissan, of Paris, has succeeded in manufacturing microscopic diamonds artificially by fusing sugar charcoal at a very high temperature in the electric furnace in various metals—iron, silver, lead, &c. In order to make the experiment a success the carbon of the sugar charcoal has to be introduced suddenly into the crucible containing the molten metal, otherwise of course it would be completely burnt away through oxidation. Immediately the metallic casing holding the sugar charcoal has been dissolved in the molten metal the crucible is removed from the furnace, and is plunged into cold water, or preferably into a bath of molten lead. This has the effect of readily cooling the exterior of the small molten mass. The crucible is then removed from the water or lead, and the cooling is allowed to be completed at a slower rate. In the process of this cooling enormous pressure is exerted by the contracting shell of solidified metal on the still molten nucleus inside containing the dissolved carbon. When this nucleus ultimately solidifies the carbon crystallising out under such conditions of intense pressure forms microscopic diamonds, some of them of the nature of black diamond, but others clear and translucent.

A second method of manufacturing diamonds artificially is that adopted by Dr. Friedlander, of Berlin. This distinguished experimenter was present at the Mexican Congress, and was intensely interested in the Oakey Creek specimens. His method is to take some splinters of the mineral olivine (a silicate of iron and magnesia, very commonly found in blue metal or basalt), and to fuse it up before the oxy-hydrogen blowpipe, stirring the molten mass the while from time to time with graphite, in the form of the carbon of a blacklead pencil. When the fused mass is cooled down he removes by means of suitable chemical reagents all the non-diamond minerals, and usually finds a small residue of true microscopic diamonds. The scientific world was at first inclined to question the accuracy of Dr. Friedlander's results, but he has since been able to amply demonstrate their correctness, and they are now generally accepted by the scientific world.

The third method of diamond manufacture is that to which Sir William Crookes has recently called attention, and it is of great scientific interest. He held that the diamond was probably formed under conditions where there was no access to free oxygen, for he contended that the presence of oxygen, even under the condition of its occurrence in molten silicates, if at a high temperature, would lead to the oxidation and subsequent destruction of diamonds. He therefore thought it probable, first, in view of Moissan's experiments, secondly from the well-known fact that diamonds have been met with in nickel iron meteorites, that the original matrix of the diamond was metallic iron. He has also drawn special attention to the following interesting fact:—"Carbon and arsenic are the only two elements that have a melting-point above their boiling-point; and among compounds carbonic acid and fluoride of silicium are the only other bodies with similar properties. That is, these solids, when highly heated, pass off direct into vapour without going through an intermediate liquid stage, as water substance, in the form of ice, does when its temperature is raised, as obviously the ice passes into water before the latter can be converted into steam. Now the melting-point of arsenic is about 1·2 times its absolute boiling-point. With carbonic acid and fluoride of silicium the melting-points are about 1·1 times their boiling-points. Applying these ratios to carbon, we find that its melting-point would be about 7460° F. With a temperature of 7460° F., a pressure of about 250 lbs. to the square inch would be the necessary melting-point pressure for carbon, as calculated, by Sir William Crookes. Any pressure, therefore, above 250 lbs. per square inch would suffice to liquefy carbon at the above temperature. In order to verify his theory that diamonds can be formed from carbon melted under the above conditions of temperature and pressure, Sir William Crookes was unable to avail himself of the electric furnace, as its maximum temperature falls distinctly below the amount postulated. As stated, however, by him, Sir Andrew Noble was able, by exploding cordite in a closed steel cylinder, to obtain a pressure of 8000 atmospheres, or 50 tons per square inch, with a temperature reaching in all probability about 9260° F. He adds:—"Here, then, we have conditions favourable for the liquefaction of carbon, and were the time of explosion sufficient to allow the reaction to take place, we should certainly expect to get the liquid carbon to solidify in the crystalline state." On subsequently examining some of the residues obtained from these closed vessels after the explosions, he succeeded in discovering microscopic crystals of true diamond. These were critically examined by Professors Bonny and Miers, who agreed with Professor Crookes that the crystals could be none other than octahedral diamonds showing characteristic cleavage, refractive index, &c. Thus, Sir William Crookes concludes that diamonds were originally formed probably at a very high temperature, and under sufficient pressure to admit of the carbon melting before it boiled, and also under conditions where there was no free access of oxygen, even in the form of silicates.

In the discussion on the genesis of the Oakey Creek diamonds, Sir William Crookes argued that the original matrix of the diamond in this case, as in South Africa, in his opinion, had been metallic iron in the first case. An obvious difficulty is the explanation of how the diamonds have become released from their iron prison. The diamonds may possibly have been set free, either by an oxidation of the iron or by the iron becoming molten while the diamond still remained solid, in which case, on account of the specific gravity of the diamond being much less than that of the iron, the diamond would at once come to the surface of the molten iron, just as a cork after being submerged

and suddenly released comes to the surface of the water. Professor David replied to Sir William Crookes that in Dr. Friedlander's experiments diamonds had actually been manufactured from graphite carbon in a molten silicate, and also that natural diamonds had been discovered in the stony meteorite of Novo Urie in Russia, and that there is therefore clear evidence to show that it is possible for diamonds to form in the presence of silicates, in spite of the fact that the latter contain oxygen.

Both Professors Bonney and Cole argued at York that even in the case of the South African diamond pipes the diamonds are not really *in situ*, but may have been derived from older masses of rock which have become churned up and largely fused in the local diamond pipe of volcanic origin. According to this contention, diamonds, when we find them now in matrix in rocks of the earth's crust, are the sole survivors of a whole group of minerals which in the long process of their transfer from deep-seated portions of the earth's crust to the earth's surface have become attached by the transporting molten rock, and dissolved in it.

According to the views of the above scientists, all diamonds have originally been formed in very old crystalline rocks, and where we now find them in a rock like the hornblende-diabase of Inverell their survival there is due to their superior infusibility, hardness, &c., as compared with these qualities in the constituent minerals of the original rock in which the diamonds grew.

Certainly in many parts of the world diamonds are of very high geological antiquity, a fact which is in favour of the view that they were derived originally from ancient crystalline rocks. For example, in one of the most famous diamond fields of India—that of Panna—the diamonds occur as transparent crystals, derived from the very ancient Vindhyan sandstones and conglomerates. Dr. Vredenburg, of the Geological Survey of India, in his recently published report on this subject, argues a derived origin for all the diamonds, not only of Panna, but as far as he knows of the whole of India. The age of these Vindhyan diamond-bearing sandstones is now, considered by Dr. T. H. Holland to be extremely ancient, referable probably to the Algonkian division of pre-Cambrian time.

In Western Australia diamonds have been discovered in a very ancient conglomerate, probably older palæozoic, worked mostly for the sake of its gold. It was found that at this mine at Nullagine, near Pilbarra, in Western Australia, the steel dies of the stampers and the stamper boxes were being constantly worn away at a comparatively rapid rate. A careful examination revealed the presence of microscopic diamonds derived from these conglomerates, and Mr. Gibb Maitland, F.G.S., the Government Geologist, is satisfied as to the genuineness of the discovery.

In South Africa also Dr. F. Hatch has shown that derived diamonds are met with on the geological horizon of the Witwatersrand conglomerates, the age of which is usually assumed to be at least as old as Devonian.

If it be conceded that all the diamonds of the world were generated in crystalline rocks of high geological antiquity, then it would follow that both in the diamond pipes of South Africa, which are newer in age than the Sydney sandstones, that is post-Triassic, as well as in the hornblende-diabase dykes or pipes of Inverell, which are later in age than our coal measures, that is post-permo-carboniferous in age, the diamonds are transported minerals, and therefore of an earlier origin, than the rocks in which they are now embedded. Of special interest in connection with this theory is the second Oakey Creek diamond exhibited to the Science Congress. This diamond was set free by weathering from the matrix. The diamond shows comparatively deep indentations of its surface, in-filled with portions of the hornblende-diabase matrix. It is not as yet certain whether these indentations are due to the removal by corrosion or resorption of minerals which crystallised out originally with the diamond, at the same time as the diamond came into being, or whether they represent negative crystals etched out of the diamond itself by the substance of the volcanic dyke in the process of the floating up of the diamond in the molten mass of the dyke to the earth's surface from considerable depths beneath. These indications at all events show that the diamonds in the hornblende-diabase of Oakey Creek are of somewhat earlier origin than their surrounding minerals, perhaps in the same sense as are the quartz crystals of rocks like rhyolites and quartz-porphyries. If, therefore, diamonds can be generated at various geological ages, and there seems to be no reasonable physical or chemical grounds for doubting this, Professor David pointed out at the Congress that it would seem just as reasonable to suppose that these Oakey Creek diamonds are really *in situ* in the hornblende-diabase, as to suppose that the quartzes of rhyolites and quartz-porphyries are practically *in situ*, and the latter view is now generally admitted to be practically established.

Much yet remains to be done in the way of further prospecting the scene of this interesting discovery at Oakey Creek, and it is to be hoped that, as the result of further study, fresh light may be thrown on the at present dark problem as to the mode of origin of the diamond, and that the find will ultimately prove to be not merely highly interesting scientifically, but also remunerative.

Already quite a number of scientists at the Congresses at York and Mexico have expressed their desire to work out details as to the mode of origin of these New South Wales diamonds. Among them may be specially mentioned the names of Professor Bonney, Professor Miers, of Oxford, Professor Offret, of Lyons, Dr. Friedlander, of Berlin, and Mr. Kunz, of the great and well-known firm of Tiffany, New York.—*Sydney Morning Herald.*

THE

APPLICATIONS OF GRIGNARD'S REACTION.*

By ALEX. McKENZIE, M.A., D.Sc., Ph.D.

INTRODUCTORY.

IN 1900 Victor Grignard (*Comptes Rendus*, 1900, cxxx., 1322) found that a vigorous action ensues when magnesium powder is added to a mixture of methyl iodide and anhydrous ether. The magnesium gradually dissolves with the formation of a clear solution from which, on evaporation of the ether, a crystalline grey hygroscopic solid is obtained. If an aldehyde (1 mol.) is added to the ethereal solution obtained from magnesium (1 mol.) and methyl iodide (1 mol.), a vigorous action again takes place with the formation of a magnesium organic compound, which, when decomposed by dilute acid, gives a good yield of the corresponding secondary alcohol.

Grignard found it possible by this method to obtain from benzaldehyde, for example, a satisfactory yield of phenyl-methylcarbinol (*Annales de l'Université de Lyon*, 1901, vi., 1), and the action is represented in the following manner:—

$$CH_3I + Mg = CH_3MgI$$

$$CH_3MgI + C_6H_5.CHO = C_6H_5.CH(OMgI).CH_3$$

$$C_6H_5.CH(OMgI).CH_3 + H_2O = C_6H_5.CH(OH).CH_3 + MgIOH.$$

Ketones, in an analogous manner, are readily converted into tertiary alcohols; thus Grignard obtained phenyl-dimethylcarbinol from acetophenone:—

$$CH_3I + Mg = CH_3MgI$$

$$CH_3MgI + CH_3.CO.C_6H_5 = (CH_3)_2C(OMgI).C_6H_5$$

$$(CH_3)_2C(OMgI).C_6H_5 + H_2O = (CH_3)_2C(OH).C_6H_5 + MgIOH.$$

In his first paper Grignard also points out that other

* A Paper read before the British Association (Section B), Leicester Meeting, 1907.

alkyl halides may be substituted for methyl iodide with equally satisfactory results.

The successful application of the new reagent for the synthesis of alcohols from esters of aliphatic monobasic acids was described in the following year (*Comptes Rendus*, 1901, cxxxii., 336). Formic esters are converted into secondary alcohols; for example, diethylcarbinol is obtained in a 73 per cent yield from magnesium ethyl bromide and ethyl formate :—

$$C_2H_5Br + Mg = C_2H_5MgBr$$

$$C_2H_5MgBr + H.COOC_2H_5 = H.C(OMgBr)(C_2H_5)(OC_2H_5)$$

$$H.C(OMgBr)(C_2H_5)(OC_2H_5) + C_2H_5MgBr =$$

$$= H.C(OMgBr)(C_2H_5)(C_2H_5) + Mg(OC_2H_5)Br$$

$$H.C(OMgBr)(C_2H_5)(C_2H_5) + H_2O = H.C(OH)(C_2H_5)(C_2H_5) + MgBrOH.$$

Acetic esters, on the other hand, yield tertiary alcohols; for example, trimethylcarbinol is obtained in an 82 per cent yield from methyl acetate :—

$$CH_3MgI + CH_3.COOCH_3 \cdot CH_3.C(OMgI)(CH_3)(OCH_3)$$

$$CH_3.C(OMgI)(CH_3)(OCH_3) + CH_3MgI \cdot CH_3.C(OMgI)(CH_3)(CH_3) + Mg(OCH_3)I$$

$$CH_3.C(OMgI)(CH_3)(CH_3) + H_2O \quad CH_3.C(OH)(CH_3)(CH_3) + MgIOH.$$

Tertiary alcohols may also be obtained from acid chlorides or acid anhydrides, the action of the magnesium alkyl halide again being assumed to take place in two phases (Tissier and Grignard, *Comptes Rendus*, 1901, cxxxii., 683). Acetyl chloride, for instance, is readily converted into trimethylcarbinol :—

$$CH_3MgI + CH_3.COCl = CH_3.C(OMgI)(CH_3)Cl$$

$$CH_3.C(OMgI)(CH_3)Cl + CH_3MgI = CH_3.C(OMgI)(CH_3)(CH_3) + MgICl$$

$$CH_3.C(OMgI)(CH_3)(CH_3) + H_2O = CH_3.C(OH)(CH_3)(CH_3) + MgIOH.$$

It was subsequently shown that aromatic halogen compounds behave like alkyl halides in forming magnesium organic compounds (*Comptes Rendus*, 1901, cxxxii., 1182). Thus phenyl bromide forms the compound C_6H_5MgBr, which, by its interaction with methyl benzoate, gives a theoretical yield of triphenylcarbinol. When magnesium phenyl bromide, however, acts on acetyl chloride, diphenylethylene, $(C_6H_5)_2C:CH_2$, is obtained in place of the alcohol $(C_6H_5)_2C(OH).CH_3$.

It was at once appreciated by students of organic chemistry that science was indebted to the French investigator for the discovery of a reagent of more than ordinary importance for synthetic purposes. As is well known, the classical work of E. Frankland and Duppa on zinc alkyl compounds opened up a highly fruitful field of research, to which important contributions were made by Wagner, Butlerow, and Saytzew. Zinc alkyl compounds are, however, difficult to manipulate on account of their spontaneous inflammability, and to this factor the comparatively limited extent of their application may be ascribed. Many of the reactions in which they play a part require weeks, or even months, for their completion, and the yields of the resulting compounds are often far from satisfactory. Magnesium organic compounds, on the other hand, are so much more easily prepared than zinc alkyl compounds; they are not inflammable on exposure to the atmosphere, and they can be manipulated with such facility that the older methods, depending on the use use of zinc compounds, have been superseded. Not only is this the case, but Grignard's reagent has been applied for the preparation of carbon compounds by methods which earlier investigators did not have at their disposal.

Grignard was not the first to attempt the substitution of magnesium alkyl for zinc alkyl compounds for synthetic purposes. Fleck (*Annalen*, 1893, cclxxvi., 134; compare Löhr, *Annalen*, 1890, cclxi., 72), working in Lothar Meyer's laboratory, showed in 1893 that magnesium methyl interacts with acetyl chloride to form trimethylcarbinol; but, in spite of the reactivity of magnesium methyl, the method presented no advantages over the use of zinc alkyls; in fact it was less convenient, since magnesium alkyls are neither volatile nor soluble in the ordinary organic solvents.

In a paper which paved the way for the Grignard reaction, Barbier (*Comptes Rendus*, 1899, cxxviii., 110) showed that the zinc in Saytzew's reaction may be replaced by magnesium, and that it is not necessary actually to isolate magnesium methyl in order to use it subsequently for synthetic purposes. It was possible to obtain dimethylheptenol, $(CH_3)_2C:CH.CH_2.CH_2.C(OH)(CH_3)_2$, from methylheptenone, $(CH_3)_2C:CH.CH_2.CH_2.CO.CH_3$, by adding methyl iodide to an ethereal solution of the ketone in the presence of magnesium.

Grignard (*Revue Générale des Sciences*, 1903, xiv., 1041) was led to study magnesium organic compounds in consequence of this work of Barbier, and of an observation of E. Frankland and Wanklyn that the zinc compound $Zn(CH_3)_2.(C_2H_5)_2O$ is formed when methyl iodide is heated with zinc and anhydrous ether in a sealed tube.

In the present account of Grignard's action the more important applications will be indicated, but no attempt will be made to give a complete *résumé* of all the work carried out in this field. Section I. deals with the various types of synthesis accomplished by aid of Grignard's reagent, Section II. with some practical details, and Section III. with the theoretical aspect of the subject.

SECTION I.

Alcohols and Phenols.

(*a*) *Secondary Alcohols.*—A large number of secondary alcohols have been obtained from aldehydes or from formic esters by the method already indicated in the Introductory Section.

(*b*) *Tertiary Alcohols.*—The mode of formation of tertiary alcohols from ketones, acid chlorides, acid anhydrides, and esters respectively has also been referred to. A large amount of work has been done in this particular branch, not only by Grignard himself, but, amongst others, by Acree, Béhal, Klages, W. H. Perkin, jun., Sachs, and Zelinsky.

Cyclic ketones behave normally towards Grignard's reagent; thus Zelinsky (*Ber.*, 1902, xxxv., 2683), converted *cyclo*pentanone, $CH_2.CH_2>CO$ (with $CH_2.CH_2$), into methyl (1)-*cyclo*pentanol (1), $CH_2.CH_2>C(OH)(CH_3)$ (with $CH_2.CH_2$), by means of magnesium methyl iodide. As an example of the application to a cyclic ester, Perkin's synthesis of terpineol, $CH_3.C=CH.CH_2>CH.C(CH_3)_2.OH$ (with $CH_2.CH_2$), from ethyl Δ^1-tetrahydro-*p*-toluate, $CH_3.C=CH.CH_2>CH.COOC_2H_5$ (with $CH_2.CH_2$), may be quoted (*Trans. Chem. Soc.*, 1904, lxxxv., 654).

Tertiary alcohols are also obtained by other methods of less importance for preparative purposes. Grignard

(*Comptes Rendus*, 1904, cxxxviii., 152; *Bull. Soc. Chim.*, 1904, [3], xxxi., 751) showed that when an ethereal solution of a magnesium alkyl halide is saturated with carbon dioxide, and the product then boiled with an excess of the reagent, trialkylcarbinols are obtained :—

$$RMgX + CO_2 = R.COOMgX$$

$$R.COOMgX + 2R'MgX = \begin{matrix} R \\ R' \\ R' \end{matrix}\!\!>\!C.OMgX + MgO + MgX_2$$

$$\begin{matrix} R \\ R' \\ R' \end{matrix}\!\!>\!C.OMgX + H_2O = \begin{matrix} R \\ R' \\ R' \end{matrix}\!\!>\!C.OH + Mg\!<\!\begin{matrix} OH \\ X \end{matrix}.$$

As will be pointed out later, a general method for making carboxylic acids is to pass carbon dioxide through the Grignard reagent and then decompose the product by water; thus Zelinsky describes the elegant method of obtaining benzoic acid by the action of carbon dioxide on magnesium phenyl iodide (*Ber.*, 1902, xxxv., 2692) :—

$$C_6H_5I + Mg = C_6H_5MgI$$

$$C_6H_5MgI + CO_2 = C_6H_5.COOMgI$$

$$C_6H_5.COOMgI + H_2O = C_6H_5.COOH + MgIOH.$$

But this type of action is not always so simple. Schroeter (*Ber.*, 1903, xxxvi., 3005; compare Meyer and Tögel, *Annalen*, 1906, cccxlvii., 55) substituted phenyl bromide for the iodide in the making of the Grignard reagent, which with carbon dioxide gave triphenylcarbinol as the main product, whilst benzoic acid and benzophenone were also obtained. In fact, the experimental conditions may be so adjusted that no benzoic acid is obtained at all (*Ber.*, 1907, xl., 1584). The formation of triphenylcarbinol is represented as follows :—

$$C_6H_5MgBr + CO_2 = C_6H_5.COOMgBr$$

$$C_6H_5.COOMgBr + C_6H_5MgBr = \begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix}\!\!>\!C\!<\!\begin{matrix} OMgBr \\ OMgBr \end{matrix}$$

$$\begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix}\!\!>\!C\!<\!\begin{matrix} OMgBr \\ OMgBr \end{matrix} + C_6H_5MgBr =$$

$$= \begin{matrix} C_6H_5 \\ C_6H_5 \\ C_6H_5 \end{matrix}\!\!>\!C.OMgBr + MgO + MgBr_2$$

$$\begin{matrix} C_6H_5 \\ C_6H_5 \\ C_6H_5 \end{matrix}\!\!>\!C.OMgBr + H_2O = \begin{matrix} C_6H_5 \\ C_6H_5 \\ C_6H_5 \end{matrix}\!\!>\!C.OH + MgBrOH.$$

Tertiary alcohols may also be obtained directly from carboxylic acids by the action of an excess of the Grignard reagent (Farbenfabriken vorm F. Bayer and Co., D.R.-P., 1906, 166898); thus phenyldiethylcarbinol, $C_6H_5(C_2H_5)_2C.OH$, is formed from benzoic acid and magnesium ethyl bromide. Metallic salts of carboxylic acids may be applied in a similar manner (*Ibid.*, 1906, 166899), thus trimethylcarbinol is formed from potassium acetate and magnesium methyl iodide.

The synthesis of tertiary amino-alcohols from esters of amino-acids has been studied more particularly by Paal (*Ber.*, 1905, xxxviii., 1686; compare *Ber.*, 1906, xxxix., 810, 2062, 4344). For example, magnesium phenyl bromide and ethyl glycollate, $NH_2.CH_2.COOC_2H_5$, form diphenylhydroxyethylamine, $NH_2.CH_2.C(OH)(C_6H_5)_2$.

After Houben (*Ber.*, 1304, xxxvii., 489) had shown that lactones when acted on by the Grignard reagent give tertiary alcohols, Paal and Hörnstein (*Ber.*, 1906, xxxix., 1361, 2823, 2827) prepared 1 : 1 - diphenyl-*d*-sorbitol, $CH_2OH.(CHOH)_4.C(OH)(C_6H_5)_2$, by acting on the acetyl derivative of *d*-gluconic lactone with magnesium phenyl bromide.

A very convenient method for preparing ditertiary glycols was employed by Valeur, who acted on esters of dicarboxylic acids with an excess of the Grignard reagent (*Comptes Rendus*, 1903, cxxxvi., 694; *Bull. Soc. Chim.*, 1903, xxix., 683; compare Dilthy and Last, *Ber.*, 1904, xxxvii., 2639); in this manner methyl oxalate and magnesium phenyl bromide yield benzpinacone, $(C_6H_5)_2C(OH).C(OH)(C_6H_5)_2$. Ditertiary glycols may also be obtained either from esters of ketonic acids or from diketones; thus Grignard (*Comptes Rendus*, 1902, cxxxv., 627) obtained the glycol $CH_3.C(OH)(C_5H_{11}).CH_2.CH_2.C(OH)(C_5H_{11})_2$ from magnesium *iso*amylbromide and ethyl levulate, $CH_3.CO.CH_2.CH_2.COOC_2H_5$; whilst Zelinsky (*Ber.*, 1902, xxxv., 2138) obtained the pinacone,—

$$(CH_3)_2.C(OH).C(OH)(CH_3)_2,$$

from diacetyl, $CH_3.CO.CO.CH_3$, and magnesium methyl iodide.

Acree (*Ber.*, 1904, xxxvii., 2753) shows that the action with a diketone may be regulated so that either one or both of the carbonyl groups react. It is possible, for example, to obtain from benzil, $C_6H_5.CO.CO.C_6H_5$, either the keto-alcohol, phenylbenzoin, $(C_6H_5)_2C(OH).CO.C_6H_5$, or benzpinacone, $(C_6H_5)_2C(OH).C(OH)(C_6H_5)_2$.

The optically active glycol, tetraphenylerythritol, $(C_6H_5)_2C(OH).CH(OH).CH(OH).C(OH)(C_6H_5)_2$, has been obtained by P. F. Frankland and Twiss by the action of magnesium phenyl bromide on dimethyl *d*-tartrate (*Trans. Chem. Soc.*, 1904, lxxxv., 1666).

(*c*) *Primary Alcohols.*—The Grignard reagent is not so useful for the preparation of primary alcohols as for the classes to which reference has been made. When a current of dry oxygen is passed into an ethereal solution of the Grignard reagent, oxidation takes place and a primary alcohol is formed when water is added (Bouveault, *Bull. Soc. Chim.*, 1903, [3], xxix., 1051), *e.g.*,—

$$C_6H_5.CH_2MgCl + O = C_6H_5.CH_2OMgCl$$

$$C_6H_5.CH_2OMgCl + H_2O = C_6H_5.CH_2OH + MgClOH,$$

the yield of benzyl alcohol being 80 per cent.

When the Grignard reagent is heated for several days with trioxymethylene the primary alcohols are obtained, sometimes in good yield; thus *n*-propyl alcohol is obtained from magnesium ethyl bromide (Grignard and Tissier, *Comptes Rendus*, 1902, cxxxiv., 107).

Ethylene oxide may also be converted into primary alcohols (Blaise, *Comptes Rendus*, 1902, cxxxiv., 551), for example, *n*-butyl alcohol is obtained from magnesium ethyl bromide (Grignard, *Comptes Rendus*, 1903, cxxxvi., 1260; *Bull. Soc. Chim.*, 1903, [3], xxix., 944).

$$\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix}\!\!>\!O + Mg\!<\!\begin{matrix} C_2H_5 \\ Br \end{matrix} = \begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix}\!\!>\!O\!<\!\begin{matrix} C_2H_5 \\ MgBr \end{matrix} \rightarrow$$

$$\rightarrow C_2H_5.CH_2.CH_2.OMgBr \rightarrow C_2H_5.CH_2.CH_2OH.$$

The action of ethylene monochlorhydrin on a magnesium organic compound takes place in two phases. The hydroxy-group is first acted on in the cold :—

$$RMgX + CH_2Cl.CH_2OH = RH + CH_2Cl.CH_2OMgX.$$

On the addition of a second molecular proportion, R'MgX, which may be different from the first, a vigorous reaction again takes place when the ether is distilled off from the mixture and the temperature gradually raised :—

$$R'MgX' + CH_2Cl.CH_2OMgX =$$

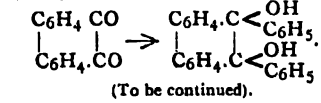
$$= MgX'Cl + R'.CH_2.CH_2.OMgX.$$

Phenylethyl alcohol, $C_6H_5.CH_2.CH_2OH$, is readily obtained in this manner from magnesium phenyl bromide (Grignard, *Comptes Rendus*, 1905, cxli., 44; *Bull. Soc. Chim.*, 1907, [8], x., 23).

(*d*) *Phenols.*—Bodroux (*Comptes Rendus*, 1903, cxxxvi., 158; *Bull. Soc. Chim.*, 1904, [3], xxxi., 33) applied for the preparation of phenols the method which Bouveault used for primary alcohols (*loc. cit.*), but the yields obtained were very small. The method appears, however, to be a general one. Thiophenols and selenophenols are formed in an analogous manner (Wuyts and Cosyns, *Bull. Soc. Chim.*, 1903, [3], xxix., 689; Taboury, *Ibid.*, 1904, [3], xxxi., 1183).

The action on *p*-quinones has been investigated by Bamberger and Blangey (*Ber.*, 1903, xxxvi., 1625), who

obtain quinols, but in small yield. Werner and Grob (*Ber.*, 1904, xxxvii., 2892) find that phenanthrene quinone and magnesium phenyl bromide give 9 : 10-dihydroxy-diphenyldihydrophenanthrene,—



(To be continued).

A REVISION OF THE ATOMIC WEIGHT OF POTASSIUM.*

I. THE ANALYSIS OF POTASSIC CHLORIDE.

By THEODORE WM. RICHARDS and ARTHUR STAEHLER.

(Concluded from p. 136).

The Drying and Weighing of the Potassic Chloride.

THE final preparation of the salt for analysis is given a special chapter to itself, because the proper execution of this feature is of very great importance, not less than the purification of the material. It is clearly useless to separate 0·001 per cent of a metallic impurity if 0·01 per cent of water is allowed to remain in the salt.

Obviously, superficial drying can not remove the imprisoned moisture in the crystals, hence they must be fused (Richards, *Zeit. Phys. Chem.*, 1903, xlvi., 189). Except in a few preliminary experiments, where a common platinum crucible was used, this fusion was conducted in a platinum boat or open bottle contained in a porcelain tube through which a current of nitrogen was passing. The experience in a number of similar cases, that the simultaneous presence of oxygen and traces of hydrochloric acid enclosed in the crystals is likely to cause perceptible corrosion of the platinum boat, was confirmed in this case; hence, an inert gas was needed. The nitrogen was prepared by the well-known method of Wanklyn, by passing air charged with ammonia over red-hot copper. The excess of ammonia was carefully eliminated by washing the gas with much dilute acid. Because fused sodic chloride was found to be essentially free from dissolved nitrogen, we did not think it necessary to fuse this very similar potassium salt in a vacuum.

Potassic chloride, although not so hygroscopic as some other salts, used in similar researches, is, nevertheless, far too hygroscopic to weigh safely when directly exposed to the air of the balance room. Its tendency to attract water was seen in perceptible crackling when the tube containing fused salt was opened in the moist atmosphere of the beaker to be used for the solution of the salt.

At first the bottling apparatus so often used in the Chemical Laboratory of Harvard College was employed to protect the fused chloride from moisture during the determination of its weight, the chloride being contained in a platinum boat protected by a glass-stoppered weighing bottle. Because, however, the weighing room was not wholly constant in temperature or in moisture, time and trouble were needed to obtain exact weighings, even although the apparatus was always weighed by substitution against a similar empty boat and bottle. The use of quartz weighing bottles proved to be no advantage, indeed, if anything, a disadvantage. In either case, if time enough were taken, satisfactory weighings could be made; but as time was especially precious, another device was used which wholly overcame the trouble.

This effective and satisfactory device consisted in the use of small weighing bottles of platinum, shaped like the long Lawrence Smith crucible, which were closed by small platinum capsules, fitting into the bottles like ground stoppers. One of these bottles, containing the potassic chloride, was supported by a loop of platinum wire in an inclined porcelain tube, and above it in the tube was placed its platinum stopper. Glass stoppers fitted into each end of the porcelain tube, which was encircled by a suitable furnace. After the potassic chloride had been dried for a long time at a high temperature, just barely fused in nitrogen, and cooled in a current of pure dry air, the stopper was shaken into place and the platinum bottle quickly removed and placed in a desiccator. This arrangement is essentially similar to the bottling arrangement of Richards and Parker, except for the additional advantages that glass is wholly eliminated and that the enclosed air-volume in the tube is much smaller. Probably the burnished platinum joint is not as tight as the ground-glass joint; but it is amply tight enough to prevent any appreciable diffusion of moisture during the very brief exposure of the tube. This was evident from the constancy of the weighings, which were made by substitution against a similar empty platinum bottle kept in a similar desiccator. The weighings were very quickly performed and were trustworthy. Before being used, the platinum bottles were repeatedly ignited with pure sublimed ammonic chloride in order to remove iron; they remained satisfactorily constant in weight during subsequent experiments, the one used for the fusion losing only 0·3 mgrm. in fourteen experiments, or on the average 0·02 mgrm. in a single experiment. In one experiment, where oxygen was present during the fusion, as much as 0·3 mgrm. was taken from the boat, the platinum being plainly visible on solution. This was, of course, not used for analysis.

All weighings, whether of this salt or of silver or argentic chloride, were made by substitution in the manner already described in other papers. (For example, see Richards and Rogers, *Zeit. Anorg. Chem.*, 1895, x., 19; also Richards and Wells, *Journ. Am. Chem. Soc.*, 1905, xxvii., 465). The balance was a short-armed insrrument made by Troemner, of the type adopted in other similar investigations; it was used only for this work and that to be described afterward. The weights were of platinised brass, carefully standardised according to the usual Harvard method. (Richards, *Journ. Am. Chem. Soc.*, 1900, xxii., 144; these weights had an average density of 8·3).

All weighings were reduced to the vacuum standard. Thus, from every apparent grm. of silver, 0·00003 grm. was subtracted, and to every apparent grm. of argentic chloride, 0·000071 was added, if the temperature was 20° and the pressure normal. Assuming the density of potassic chloride to be 1·995, the similar correction for this salt was + 0·000456. Changes in temperature and pressure occasionally caused slight but usually inessential changes in these corrections (Richards and Wells, *Journ. Am. Chem. Soc.*, 1905, xxvii., 465).

The wholly colourless transparent fused salt was dissolved in the purest water in a covered beaker of Jena glass under a tightly fitting bell-jar. The solution was always perfectly clear, except in the rejected case already cited and one other similar one. After this solution had been very thoroughly washed away and used for analysis, the platinum weighing bottle was heated for a short time in another crucible, and weighed in preparation for another analysis. The constancy of these weighings has already been discussed.

The details of preparation having been described, the analytical methods themselves must be indicated. The problem was, as in the case of sodium, to determine the amount of chlorine present, the weight of potassium being found by difference. Both of the previously used methods for finding the amount of chlorine were used, and the details are so much like those discussed by Richards and Wells (*loc. cit.*) that much may be assumed as understood. For a full understanding of the present work, that upon sodium should be read in connection with it.

The two methods for the determination of chlorine, namely, the weighing of the precipitated argentic chloride on the one hand, and the discovery of the equivalent amount of silver on the other, are discussed below in order.

* *Publication* No. 69, Carnegie Institution of Washington.

The Precipitation and Weighing of Argentic Chloride.

For purposes of analysis, the solution of potassic chloride was carefully and completely transferred to a large Jena glass Erlenmeyer flask with a finely ground glass stopper, and diluted to the volume of a litre or more. To this in the dark-room under the red light was added exactly the calculated weight of argentic nitrate, never more concentrated than one-fiftieth normal; and the mixture was shaken for a short time in order to aggregate the great mass of the precipitate. Because of the absence of an excess of argentic nitrate, the danger of the occlusion of this salt was slight. On the following day the supernatant liquid was usually quite clear, and to it now was added the excess of perhaps 0·05 grm. of argentic nitrate needed for complete precipitation. This method of treatment was found to be more satisfactory than the immediate addition of all the argentic nitrate at once, as in this case long and tiresome shaking and washing of the precipitate was needed to eliminate wholly the occluded argentic nitrate. Thus was one of the chief difficulties met by previous experimenters almost entirely overcome. It was shown in the paper on sodium that the simplest test for the presence of argentic nitrate is the appearance of the argentic chloride after fusion, even a small trace of nitrate causing a perceptible grey-violet cloudiness. In all cases when the above precaution was used the fused mass was perfectly clear and transparent. This is, however, an anticipation of the later part of the process; the collection, ablution, and desiccation of the precipitate should first be described.

In preliminary experiments, the Gooch perforated platinum crucible with asbestos mat was used with all the precautions previously adopted in this laboratory. In this way it is certain that good results may be obtained; but the necessary second filtration of the filtrate in order to collect the traces of disintegrated asbestos is a tiresome process. On this account preliminary experiments were made with Gooch crucibles provided with a smooth and burnished mat of platinum sponge, as prepared by Heraeus. (See *Zeit. Angew. Chem.*, 1901, xiv., 923; a number of experimenters have recommended and used a mat of platinum sponge in a Gooch crucible, but Munroe was probably the first, *Journ. Analyst Chem.*, 1888, ii., 241; also CHEMICAL NEWS, 1885, lviii., 101). Such crucibles are named by him after Neubauer, but might more properly be called Gooch-Munroe crucibles. In these tests it was found that such crucibles, as a matter of fact, answer very well for the purpose in hand if certain special precautions are taken. It is not permissible to ignite them at a high temperature, unless the precipitate also is to be ignited at a high temperature. A crucible brought to constant weight at 150° was found to lose 0·15 mgrm. on ignition, probably because of loss of previously adsorbed water. Moreover, when a dilute solution of argentic nitrate, potassic nitrate, and nitric acid, such as remains after an analysis, was passed through the filter, and this was five times washed with water, and dried at 150°, yet 0·15 more was gained, probably due to adsorbed salts. Very thorough washing after this brought the crucible back to its original weight after drying at 150°.

These experiments showed that the washing of the platinum sponge must be very thorough, and that a definite temperature must always be used for drying. Other experiments showed that constant weight could always be obtained, if these conditions were fulfilled.

It is well known that argentic chloride sometimes clings to a platinum surface, and always shrinks much on drying. On this account the somewhat delicate upper surface of the sponge was protected by a closely fitting disk or diaphragam of platinum punched with many fine holes. This diaphragm, merely laid upon the top of the sponge at the base of the crucible, was easily loosened with the precipitate, and formed an effectual protection for the sponge. After this was done, no platinum was ever lost from the upper surface, and none was ever carried away mechanically from below in the wash-water.

In spite of the presence of the disk, small particles of argentic chloride always clung here and there to the sponge. As a possible means of removing these when preparing for a new analysis, potassic cyanide was tested. It was found, however, that not only was this salt adsorbed by the sponge, but that in the presence of air platinum was dissolved even to the extent of a mgrm.—a fact not new, but none the less pertinent. Thiosulphate was not tried, because sulphur was an impurity little wished. Finally, while ammonia for a short time was inefficient, this liquid, when concentrated and applied for twelve hours or more, dissolved every trace of the silver salt without harming the crucible.

The technique of the Gooch-Munroe crucible having thus been mastered, this utensil was used with satisfaction as a means of collecting and weighing the precipitate in hand. The latter was first washed often by decantation, as is recounted below, and finally on the filtering crucible, which was dried to constant weight by a temperature gradually rising to 150°. After careful weighing, the main mass was separated from the clinging platinum disk, and was carefully fused in porcelain, as has often been described. The accurately determined loss on fusion, amounting sometimes to a mgrm., was calculated from the part to the whole, and applied as a correction to the total weight of the precipitate.

This weight, even as thus corrected, did not, however, exactly represent the total in weight of the chlorine, as some of the argentic chloride was dissolved by the wash-water. The ablution had been conducted in three stages, just as in the often-cited investigation of sodium. The first stage included the mother-liquor and first five wash-waters, containing intentionally as much argentic nitrate as the mother-liquor, and added to remove the greater part of the potassic nitrate. This first quantity of liquid was entirely free from chlorine in every accepted analysis, as was shown by careful testing in the nephelometer, and so was at once cast aside.

The second stage of washing was conducted with very dilute nitric acid, and yielded 0·5 or 0·6 litre of a very dilute solution of mixed nitric acid and argentic chloride and nitrate. The traces of chloride which it contained were carefully estimated in the nephelometer after addition of excess of argentic nitrate.

The third stage of the washing, also conducted with pure water acidified with nitric acid to prevent colloidal irregularities, yielded a litre or more of liquid containing much argentic chloride. The analysis of this liquid constituted a very important part of the work and gave much trouble.

In order to be as certain as possible of the weight of chlorine it contained, this liquid was tested in five cases according to two very different methods. The first of these consisted in evaporation of the solution under diminished pressure and actual weighing of the precipitate, and the second consisted in a new modification of the nephelometer test. Although the latter evidently gave the more satisfactory results, the former is worthy of brief discussion, because its outcome certainly represents the maximum value.

In order to carry out these two parallel quantitative tests, the collected wash-water was divided into two parts; and the larger part, about 90 per cent of the whole, was evaporated under low pressure at 50° in a specially made Jena glass 2-litre flask with a glass stopper. In the course of this evaporation the argentic chloride began to separate out when the volume had been reduced to about 0·2 litre, if 2 mgrms. of the salt were present—a fact agreeing well with the recent observations concerning this solubility (see, for example, Böttger, *Zeit. Phys. Chem.*, 1906, lvi., 93). The dried residue was dissolved in a very little ammonia freshly distilled in platinum, and washed into a small precipitating flask, where it was re-precipitated with excess of argentic nitrate and nitric acid. This trace of precipitate was collected and weighed on a fresh Gooch-Munroe cruclb'e in the same way as the larger mass. The results

are given below in comparison with those obtained from the same solutions by the nephelometer.

An important modification was introduced into the nephelometric determination. One of us has repeatedly pointed out that in order to obtain satisfactory results with this instrument the solution to be tested and that used as the standard of comparison must be treated in exactly the same way (*Am. Chem. Journ.*, 1904, xxxi., 242; 1906, xxxv., 509). Hence, the use of a ground-glass plate as a standard of comparison is a very questionable proceeding (Wells, *Am. Chem. Journ.*, 1906, xxxv., 99). It appears that the precipitation of argentic chloride from solutions of this salt differ perceptibly in mechanism from the precipitation of the same substance from other chloride solutions, even when argentic nitrate in great excess is used in each case (Richards and Wells, *Pub.* 28 Carnegie Inst., 1905, xxviii., *Journ. Am. Chem. Soc.*, 1905, xxvii., 485). Accordingly, in order to secure a perfectly satisfactory comparison, both precipitates must be dissolved in ammonia and re-precipitated. The precipitate then appears in each case in precisely the same condition, and yields trustworthy results.

The present tests were carried out in the following manner:—Two test-tubes of precisely the same volume (0·025 litre) were provided. Into one of these was placed 0·015 litre of the wash-water, and into the other, serving as the standard of comparison, a like volume of water containing about as much carefully measured chlorine (in the form of potassic chloride) as was present in the first. Into each was now run 5 molecules of a three-hundredth normal solution of argentic nitrate. The solutions were stirred with a platinum stirrer, previously cleansed with ammonia and the purest water. After five minutes, the precipitates were well formed; they were then both dissolved with the help of a millilitre of freshly distilled ammonia, and re-precipitated with a slight excess of nitric acid, being filled to similar marks near the top of the tubes. The two cloudy solutions, thoroughly stirred, were allowed to stand and compared optically in the nephelometer in the usual way.

The following table compares the results obtained by the two methods. The varying solubility of the halide in the wash-water was mainly due to difference in temperature at the time of the ablution.

The Comparison of Weights of Argentic Chloride found Nephelometrically and by Evaporation.

Experiment No.	Volume.	Weights of argentic chloride.		
		By evaporation.	By nephelometer.	Diff.
	Litres.	Mgrms.	Mgrms.	Mgrm.
10.	1·45	3·96	3·12	−0·84
11.	1·88	3·82	3·22	−0·60
12.	1·18	2·59	1·97	−0·62
13.	0·90	1·70	1·35	−0·35
14.	1·00	1·74	1·45	−0·29

Thus, the nephelometer always indicated less argentic chloride than the gravimetric process. At first the nephelometer was suspected, but the steadily diminishing difference between the two series of results indicated that they were approaching the point where they would indicate the same values. As the nephelometric treatment was invariable, but, on the other hand, the evaporating flask might easily be attacked, it seemed probable that the decreasing difference exhibited by the figures was due to something added to the weight of the precipitate from the latter source. Apparently, as is reasonable, the flask was less and less attacked as it continued in use.

For this reason the gravimetric results were wholly rejected, and the nephelometric ones alone used in the calculation of the final results.

The Ratio of Potassic to Argentic Chloride.

The final results of the series of analyses discussed above are recorded in the following table. A number of preliminary experiments are omitted from this table, since it is clear that no doubtful or imperfectly executed experiment should find a place in such a table of final data. The list is nearly consecutive, however, as but few experiments met with misfortune after the processes had been mastered. The original numbering of the experiments is retained; they were recorded in the notebook in chronological order. All the argentic chloride referred to in this table was clear and colourless; a fact which is one of the best proofs that it was free from argentic nitrate or from organic dust.

Final Series of Determinations of the Ratio KCl : AgCl.

No. of analysis.	Preparation of KCl.	Weight of fused KCl in vacuum	Weight of fused AgCl in vacuum.	AgCl : KCl = 100·000 : *x*.	Atomic weight K if Cl = 35·473.
		Grms.	Grms.		
13.	*a*	4·36825	8·3986	52·012	39·114
14.	*a*	5·56737	10·7038	52·013	39·115
15.	*a*	6·41424	12·3323	52·012	39·114
20.	*b*	3·27215	6·2913	52·011	39·112
31.	*b*	4·83028	9·2870	52·011	39·112
		Average		52·0118	39·1134

This result will be discussed after the next series has been presented. It has a probable error, calculated by the method of least squares, of only about 0·0004; accordingly, further repetition was deemed unnecessary.

The Ratio of Potassic Chloride to Silver.

In this series of experiments, weights of the purest silver equivalent to entirely new portions of fused potassic chloride, as calculated from the preceding table, were dissolved in nitric acid, and the two equivalent solutions were mixed. Great care was used. The presence of an excess of silver or of chlorine was then determined with the nephelometer, exactly according to the details of manipulation adopted by Richards and Wells, whose accounts should be consulted for particulars. The table below contains the final results; the preliminary practice experiments are omitted for the same reason as before.

Final Series of Determinations of the Ratio Ag : KCl.

No. of analysis.	Preparation of KCl.	Weight KCl in vacuum.	Weight Ag in vacuum.	Ratio Ag:KCl = 100·000 : *x*.	At. wt. of K if Cl = 35·473.
		Grms.	Grms.		
19.	*a*	3·88074	5·61536	69·109	39·117
21.	*a*	7·44388	10·77156	69·107	39·114
24.	*c*	5·00681	7·24514	69·106	39·113
27.	*e*	5·04833	7·30515	69·107	39·114
30.	*e*	8·19225	11·85412	69·109	39·117
32.	*d*	4·99795	7·23230	69·106	39·113
33	*f*	5·16262	7·47042	69·107	39·114
		Average		69·1073	39·1145

In this case the "probable" error is even somewhat less than before, being under 0·0004.

Discussion of Final Results.

Thus, two results have been obtained, giving for the atomic weight of potassium the value 39·113 by reference to argentic chloride, and the value 39·114 by reference to pure metallic silver. The close agreement of these results is an important evidence of their verity, and a striking confirmation of the new atomic weight of chlorine found by Richards and Wells. The atomic weight of chlorine is very simply calculated from the results of the two series above as follows: — Cl = (69·1073/52·0118—1·00000) 107·93 = 35·475—very near the most likely value, 35·473.

Such difference as exists is probably due to the slight remaining trace of occlusion of foreign salts by the argentic chloride. In the present case this source of error was eliminated more successfully than ever before, hence the agreement between the two values of the atomic weight of potassium was closer than usual.

It may be noted that the difference between the new

value and the old value of Stas is somewhat less than in the case of sodium. Stas's results with potassic chloride led him to the value 39·146, about 0·032 higher than the new result, while with sodic chloride the difference was 0·042. A large part of this difference in each case is due to Stas's error in the atomic weight of chlorine; corrected for this error, the differences become 0·016 and 0·026 respectively. The differences are to be referred to the same causes in this case as in the others—namely, to Stas's incomplete knowledge concerning solutions of argentic chloride, to his practice of dropping solid salt into the precipitating solution, and to the presence in his preparations of traces of impurity taken from containing vessels. In the case of potassium one or more of these errors must have been less than in the case of sodium.

The results of Richards and Archibald, although very few in number and not intended to figure in a discussion of this kind, were somewhat better—probably because solid salt was never used directly in precipitation. Assuming the present research to yield the true value, their errors in the two series were, respectively, 0·009 and 0·014. The result of Archibald alone for the ratio of silver to potassium chloride was about the same amount (0·008) different from the present value; but his result for the other ratio was less satisfactory, having an error of 0·021, even greater than Stas's. These differences are not surprising, because less was known at that time than at present concerning the behaviour of argentic chloride in solution.

Although the present paper presents strong evidence that the atomic weight of potassium is really as low as 39·114, more remains to be done. It would have been desirable to have used also some other wholly different method of preparing potassic chloride, and, moreover, to have evaporated large samples of the salt in nitrogen in order to discover a possible non-volatile residue. It is very doubtful if these additional experiments would have altered the present result, especially considering the precautions taken in the work, and the result of the following research; but, nevertheless, it is planned to pursue these matters further.

Even when every conceivable precaution is taken, a single salt is not an adequate basis for the certain decision of an atomic weight. For this reason a parallel investigation on potassic bromide was simultaneously in progress at the Chemical Laboratory of Harvard College. The next communication, describing this other research, must be considered in connection with the work which has just been described. As will be seen, excellent confirmation of the present work is afforded by the work with the bromide.

Summary.

This investigation concerning the quantitative composition of potassic chloride resembled in many respects the recent investigation of Richards and Wells on sodium.

In several details, however, improvements were introduced which effected a considerable saving of time and a perceptible gain in accuracy.

The precautions necessary for the accurate use of the Gooch-Munroe perforated crucible were ascertained; its employment was found to be advantageous.

Platinum weighing bottles with conical ground-platinum stoppers were used instead of boats and glass tubes for weighing the potassium salt.

Occlusion of argentic nitrate by the precipitated chloride was diminished by allowing the latter to stand for a long time in a solution containing neither excess of silver nor excess of soluble chloride, and by adding more argentic nitrate only after the precipitate had assumed a fairly permanent condition of aggregation.

The nephelometric estimation of small amounts of suspended argentic chloride was increased in accuracy by redissolving in ammonia both of the opalescent precipitates to be compared and re-precipitating in order to equalise the conditions.

As final results, the outcome of twelve experiments, 100·000 parts of silver were found to correspond to 52·0118 parts of potassic chloride, and 100·000 parts of argentic chloride were found to correspond to 69·1073 of this salt.

The corresponding values for the atomic weight of potassium (if silver is assumed to be 107·930 and chlorine 35·473) are 39·1134 and 39·1145, in unusually close agreement.

A METHOD FOR THE ESTIMATION OF IRON IN PRESENCE OF TITANIUM.

By F. A. GOOCH and H. D. NEWTON.

For analytical purposes, a ferric salt in solution is most easily and conveniently reduced to the ferrous condition by the action of zinc; and where many determinations of iron are to be made, the use of the well-known reductor, first proposed by Jones ("The Chemical Analysis of Iron," Second Edition, p. 203), and described in simple form by Blair ("The Chemical Analysis of Iron," Sixth Edition, p. 94), yields accurate results very rapidly. The use of zinc, whether in the flask or in the reductor, has, however, been precluded when the ferric salt is accompanied by titanic acid, for this substance is reduced with the iron and subsequently oxidised by the permanganate in the titration process. When, therefore, titanium is present with the iron, it has been customary to have recourse to other methods of reduction. In this event, either hydrogen sulphide or sulphur dioxide is substituted for the zinc to bring about the reduction of the ferric salt, while titanic acid is not reduced by these reagents; but the removal of the excess of hydrogen sulphide or of sulphur dioxide from solution without oxidation of the ferrous salt is not an easy or rapid process.

The present investigation was undertaken for the purpose of adapting the ordinary convenient process of reducing the ferric salt by zinc to the estimation of iron in presence of titanium. It is obvious that to solve this problem it is only necessary to find and employ some reagent which shall be neutral toward the ferrous salt but capable of re-oxidising the titanium compounds formed by the reducing action of the zinc and without action on the permanganate. Compounds of silver, copper, or bismuth oxidise very easily the reduced titanium salt; but the use of a compound of silver is precluded by the fact that it oxidises also the ferrous salt to some extent as well as the titanium salt. Cupric salts and pure bismuth oxide prove, however, to be without action upon the ferrous salt.

For the work to be described, ferric oxide was prepared from pure ferrous oxalate and converted to ferric sulphate, and a solution of this salt was made up of convenient strength and standardised by reducing the iron with zinc in a small flask, as recommended by Blair ("The Chemical Analysis of Iron," Sixth Edition, p. 225), and titrating with potassium permanganate. Titanium sulphate was prepared in solution by digesting pure titanic acid in concentrated sulphuric acid and diluting the filtered solution to known volume.

In preliminary experiments it was found that the violet colour of the solution containing the titanium compound produced by the action of zinc upon the titanium sulphate was discharged by adding a little cupric sulphate to the solution and heating, and, after filtering, a drop of potassium permanganate gave its characteristic rose tint to the solution. It was found also that when cupric oxide was added to a similarly reduced solution of the titanium salt the characteristic colour vanished on shaking the solution. The following table contains the results obtained in titrating with potassium permanganate the ferrous salt left after reducing by zinc in small flasks carefully measured amounts of ferric sulphate and titanium sulphate, treating the mixture thus obtained with cupric sulphate or with

cupric oxide, and filtering off the reduced copper and cuprous salt.

TABLE I.

Fe_2O_3 taken. Grm.	TiO_3 taken. Grm.	Fe_2O_3 found. Grm.	Error.	
0·1375	0·1	0·1378	+0·0003	(a)
0·1375	0·1	0·1374	−0·0001	
0·1375	0·1	0·1377	+0·0002	
0·1375	0·1	0·1378	+0·0003	(b)
0·1375	0·1	0·1378	+0·0003	
0·1375	0·2	0·1382	+0·0007	

(*a*) Treated with $CuSO_4$. (*b*) Treated with CuO.

So it appears that either cupric sulphate or cupric oxide may be used to re-oxidise the salt of titanium reduced by zinc, without affecting appreciably the ferrous salt in solution.

Similar experiments in which bismuth oxide was substituted for the copper oxide are recorded in Table II. To the measured amount of ferric sulphate and titanium sulphate contained in a small flask, provided as usual with the funnel valve, zinc was added, and the reduction effected in the ordinary manner. The titanium salt appears to act catalytically in this process, so that reduction goes on more easily and with less expenditure of zinc than in the similar reduction of the ferric salt taken by itself. After the zinc had disappeared, the solution, of characteristic violet colour, was cooled in the flask, treated with a little bismuth oxide, gently shaken, filtered from the excess of bismuth oxide and the precipitated bismuth into about a litre of cold water, and titrated with standard potassium permanganate.

In Table III. are given the results obtained when reduction was effected by passing the ferric sulphate solution through a column of amalgamated zinc, 20 to 30 mesh, used in the simple form of reductor recommended by Blair (*loc. cit.*). The receiving flask was kept cool in running water, a small amount of bismuth oxide added, the flask shaken, and allowed to stand a few minutes, and filtration made with the aid of the suction pump. In the cold solution free from dissolved oxygen there is little danger of re-oxidation of ferrous sulphate, as has been shown by Peters and Moody (*Am. Journ. Sci.*, xii., 367).

TABLE II.

Ferric sulphate. Cc.	TiO_3. Grm.	$KMnO_4$. Cc.	Fe_2O_3 taken.	Fe_2O_3 found.	Error.
10	0·04	12·84	0·0993	0·0992	−0·0001
10	0·06	12·85	0·0993	0·0993	0·0000
10	0·08	12·90	0·0993	0·0997	+0·0004
10	0·1	12·90	0·0993	0·0997	+0·0004
10	0·1	12·89	0·0993	0·0996	+0·0003
10	0·1	12·85	0·0993	0·0993	0·0000
10	0·1	12·80	0·0993	0·0989	−0·0004
10	0·1	12·90	0·0993	0·0997	+0·0004
10	0·2	12·90	0·0993	0·0997	+0·0004
10	0·2	12·89	0·0993	0·0996	+0·0003
10	0·2	12·90	0·0993	0·0997	+0·0004
20	0·1	25·70	0·1986	0·1986	0·0000

TABLE III.

40	0·01	46·80	0·3943	0·3943	0·0000
40	0·02	46·79	0·3943	0·3942	−0·0001
40	0·04	46·80	0·3943	0·3943	0·0000
40	0·06	46·83	0·3943	0·3946	+0·0003
40	0·1	46·75	0·3943	0·3939	−0·0004
40	0·1	46·82	0·3943	0·3945	+0·0002
40	0·1	46·78	0·3943	0·3941	−0·0002
40	0·1	46·80	0·3943	0·3943	0·0000
40	0·1	46·75	0·3943	0·3939	−0·0004
40	0·1	46·80	0·3943	0·3943	0·0000
40	0·2	46·77	0·3943	0·3940	−0·0003
40	0·2	46·81	0·3943	0·3944	+0·0001
40	0·2	46·85	0·3943	0·3947	+0·0004

These results show plainly that the ordinary process of reducing ferric salts by means of zinc, either in the flask or in the reductor, may be made applicable in presence of titanium compounds by adding copper oxide or preferably bismuth oxide to the reduced solution, and filtering before titrating with potassium permanganate.—*American Journal of Science*, xxiii., p. 365.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xl., No. 12, 1907.

New Yttria-niobium Mineral.—Otto Hauser.—The author has analysed a mineral which was described as orangeite, similar to euxenite. Chemical analysis, however, showed that it is a niobate of yttrium, allied in composition to fergusonite, although it differs from the latter in its mineralogical properties and it contains titanic acid and no uranium. It is characterised by its abnormally high loss on ignition. The analysis of the mineral gave the following results:—

Nb_2O_5, TiO_2	45·23
$Y_2O_3, La(Ce, Di)_2O_3$	41·19
Al_2O_3	0·80
Fe_2O_3	2·51
CaO	1·80
PbO	0·19
SnO_2, ThO_2..	Traces
Loss on ignition..	8·40
	100·12

No other elements are present, so that its composition is remarkably simple for a niobate. Among the components of the yttrium earths the colourless earths are predominant, and of the erbium earths dysprosium and holmium are relatively abundant. Terbium is present only in small quantities, and minute traces only of praseodymium can be detected.

Iodometric Determination of Mercury.—E. Rupp.—The author has already reported that the mercuric ion can be precipitated as metal by alkaline formaldehyde solution and again dissolved by N/10 iodine. The reduction must be carried out at the temperature of the water-bath if the precipitation with alkali is performed directly, while the room temperature is sufficient if the mercury salt is first converted into mercury iodide-potassium iodide by the addition of potassium iodide. The reduction then takes place very quickly, but the liquid has to be thoroughly shaken for one to two minutes. If this is not done, the results obtained are low, because some of the mercury is converted into acetate on acidifying with acetic acid, and it is then incapable of reacting with iodine.

Melting-point of Pure Tungsten.—H. v. Wartenberg.—A satisfactory method of determining the melting-point of tungsten, which is known to lie in the neighbourhood of 3000°, can be carried out with Geissler tubes with Wehnelt's cathode. It is then found that the "black temperature" of tungsten is 2650 ± 20° C., while the true melting-point is at least 2800° C., and probably does not exceed 2850° C. The fused tungsten on cooling looks like highly polished platinum, is easily marked with a knife, but breaks on the application of greater pressure. The density of solid tungsten is greater than that of the fused metal, in which there are interstices.

Separation of Tellurium from the Heavy Metals and the Formation of Cupric Acid.—Bohuslav Brauner and Bohumil Kuzma.—When tellurium is precipitated by sulphurous acid in presence of heavy metals it carries down with it greater or smaller quantities of the following metals:—Mercury, lead, bismuth, copper, cadmium, arsenic, antimony, thallium, &c. From quantitative experiments performed with copper, the authors find that

the amount of copper carried down is greater the greater the amount of it present. Smaller quantities of bismuth and antimony are carried down than of copper. To separate tellurium from the above heavy metals it is best to convert it into the ion TeO_4'' by means of ammonium persulphate, and the telluric acid may then be reduced by means of hydrochloric acid and subsequent precipitation with sulphurous acid, and this method can be employed to separate very small quantities of the heavy metals from tellurium. When the precipitates, containing copper which they have carried down, are oxidised with nitric acid, the solution is evaporated, and the residue taken up with caustic potash, it completely dissolves. If the solution is oxidised with ammonium persulphate, an intense red colouration is produced, which is generally ascribed to cupric acid. Since neither tellurium alone, nor tellurium in presence of another element than copper, gives this red compound on oxidation with persulphate, the unstable cupric acid must be able to exist only as a constituent of a negative complex telluro-cupric acid. Under different conditions salts of the following composition can be prepared:—

$$2K_2O.Cu_2O_3.3TeO_3+xAq,$$
$$2K_2O.CuO.2Cu_2O_3.3TeO_3+xAq.$$

MISCELLANEOUS.

The Sir John Cass Technical Institute.—The new Session will commence on Monday, September 23rd. The work of the several departments has been considerably re-organised since last year. Apart from systematic courses in Physics, Mathematics, and Chemistry, in which provision is made for students preparing for Degrees of London University in Experimental Science, special courses of instruction will be given in Physical Chemistry, Brewing and Malting, and in several branches of Advanced Physics, including Radio-activity. The courses in Physical Chemistry will include General Physical Chemistry, Electro-chemistry, and a laboratory course of practical work; the instruction in Brewing and Malting will also include laboratory work of a technical character, in addition to a course of lectures designed for those engaged in the Brewing and Malting industries, in which full attention will be given to modern methods of work. The teaching in Metallurgy, which for the past four years has formed a distinctive part of the work of the Institute, has now been established as a separate department, and a full graded curriculum, extending over three years, is provided, which includes advanced instruction in the Metallurgy and Metallography of the most important metals and the analysis of Fuel and of Gas for technical purposes, in addition to systematic courses of lectures and laboratory work in general Metallurgy.

Electrical Measuring Instruments.—Messrs. Archibald Constable and Co. beg to announce that they will publish during the autumn a new and comprehensive work on Electrical Measuring Instruments (recorders, meters, &c.), by Mr. Kenelm Edgcumbe, M.I.E.E.

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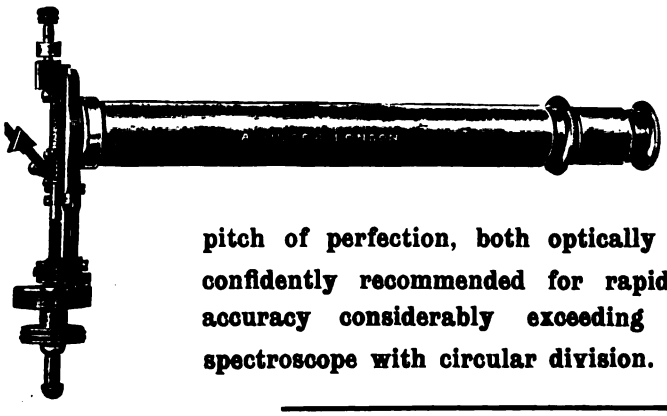

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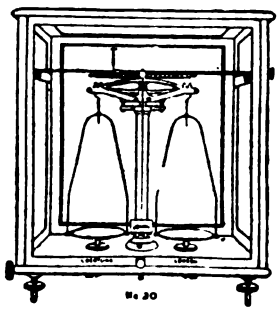

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THE DEPOSITION OF METALLIC SILVER UPON GLASS.

Short Studies in Chemical History (II.).*

By F. D. CHATTAWAY.

Mirrors made of polished metal or of hard polished stone have been known from very early times, and references to them are scattered through ancient literature. The use of glass mirrors with a reflecting surface formed by a coating of gold-leaf, lead, or tin, or even of pitch, is also of considerable antiquity.

Looking-glasses coated with an amalgam of quicksilver and tin first came into use about the middle of the fifteenth century, but it is not known by whom they were originally made. Their manufacture was introduced into Venice in the year 1507, and was carried on with such success that it became an important source of revenue to the Republic, though it is probable that the industry was established earlier in Germany and Flanders.

The actual details of the process used were for long carefully guarded as a trade secret, and the first explicit instruction for carrying it out were given in the middle of the sixteenth century by Johannes Porta, an Italian. He directs that a thin sheet of tin is to be taken and spread carefully on a flat table, a little mercury is to be poured upon it, and rubbed about with a hare's foot till the whole surface is coated and silvery in appearance. On this a clean sheet of white paper is to be laid, and above the paper the carefully cleaned sheet of glass. The paper is then to be drawn out, and the glass pressed down by weights until the excess of mercury has flowed away.

The manufacture of mirrors in this manner did not become well established in Northern Europe till the middle of the eighteenth century, and reached its most extensive development during the latter half of last century.

The operation of coating glass with tin amalgam is still carried out in much the same way. A perfectly smooth sheet of tin-foil, free from all faults and somewhat larger than the glass to be covered, is spread upon a flat well-polished marble or slate slab, and mercury brushed over it till the whole surface is unformly amalgamated. Wooden laths or glass strips are laid on three sides of the sheet and kept down by weights, while more mercury is added till the tin-foil is covered to a depth of from 4 to 6 mm. A brilliant surface is next produced upon the fluid metal by skimming off the grey coating of oxide with a wooden rod. The sheet of glass, previously very carefully cleaned, is then pushed forward horizontally from one side of the table with its longest edge foremost, so that this edge is always kept dipping below the surface of the mercury, but not touching the tin-foil. By this means the plate is brought into intimate contact with the metal, and dust and air are totally excluded, while if it were let down perpendicularly more or less of both would certainly be enclosed between the glass and the amalgam. To get rid of the excess of quicksilver the upper surface of the glass is next loaded with cast-iron or stone weights covered with flannel or forced down by screws to a pressure of about 1 kgrm. per 7 sq. cm., and the table slightly inclined diagonally. After about four minutes the plate is still more weighted, and allowed to remain thus for twenty-four hours, the inclination being gradually increased to about 10 to 12 degrees. It is then turned over with the coated face uppermost, removed from the table, and gradually raised to an upright position, in which it is kept for three to four weeks. At the end of that time there is left upon the glass a dry hard coating of tin amalgam, which is usually varnished to protect it from accidental damage. The mercury which runs off during the weighting can only be used again after having been completely freed from tin by distillation.

This process takes a long time to complete, and is, moreover, often subject to failure; the plates frequently break under the pressure of the weights, and when they are set vertical drops of mercury sometimes trickle down, producing curved streaks technically called "worms," so that it becomes necessary to re-coat the whole mirror. The amalgam also is liable to become crystalline and is further easily injured by carriage.

The manufacture of mercurial mirrors is attended by the still greater drawback that the workpeople employed very frequently suffer from mercurial poisoning. By strict regulations and the most scrupulous cleanliness this danger can be reduced to a minimum, but it cannot absolutely be guarded against.

At the present time, owing to the invention by various chemists of methods of depositing silver upon glass, mercurial amalgam mirrors are not extensively manufactured, except in France, where the slight yellow tint of silver mirrors is regarded as objectionable.

In England the process is practically given up, and for years the Home Office has not had notified to it a case of mercurial poisoning among mirror makers.

The abandonment of mercurial mirror making with its grave dangers to health affords an excellent illustration of the way in which apparently insignificant chemical discoveries can transform important industries.

When towards the middle of last century the study of organic compounds began to attract widespread attention among chemists, it was soon found that many substances were able to throw down silver from solutions of its salts and form brilliant metallic films on the surface of the glass. Liebig was the first to notice this. In his paper "On the Products of the Oxidation of Alcohol" (*Annalen*, 1835, xiv., 133), announcing the discovery and isolation of the compound which he named aldehyde, he states that if a solution of silver nitrate, to which some drops of ammonia have been added, is warmed with the new compound, the silver oxide is immediately reduced, and that the reduction is accompanied by a peculiar phenomenon, the metal attaching itself to the glass in the form of a thin reflecting layer.

The first attempt to use such a reduction of silver in the manufacture of mirrors was made by Thomas Drayton, of Brighton, who in 1843 protected a process by a patent.

Drayton's specification (A.D. 1843, No. 9968), which is dated November 25th, 1843, states:—"The invention consists in causing silver to be deposited on to glass from a solution of silver by deoxidising the oxide of silver in solution in such a manner that the precipitate of silver will adhere to the glass without any previous coating of the glass with metallic or other substances. I would first remark that the invention is applicable in the manufacture of looking-glass and in other cases where it is desired to have glass coated with silver. It is well known that in silvering glass in the making of looking-glasses, as at present practised by the use of quicksilver, the process is very unhealthy, and it is an important feature in this invention that this injurious and unhealthy process is dispensed with, and the glass is coated with silver deposited from a solution of silver, giving a more beneficial result and a very beautiful effect. My process is as follows:—I take at the rate of one ounce of coarsely pulverised nitrate of silver—that which I generally employ is the lunar caustic of commerce—and mix it with half an ounce of spirits of hartshorn; to these I add two ounces of water, and let the mixture stand twenty-four hours; then filter the same (preserving the deposit on the filter, which is silver). I then add to the filtered liquor three ounces by measure of spirit. I prefer spirits of wine at about 60° above proof, or

* The first of this series, "On the Determination of the Composition of Nitrogen Iodide," appeared in Chemical News, vol. xciv., p. 130.

naphtha. I then add from twenty to thirty drops of oil of cassia. The mixture, after having remained for five or six hours, is ready for use, and I have found it desirable not to keep it more than twenty-four hours after the oil of cassia has been added thereto; but the mixture before the addition of the oil of cassia appears to improve by keeping. When the proper time has elapsed after the addition of the oil of cassia, the mixture is to be applied in the following manner:—The glass intended to be silvered having been placed in a horizontal position, I form a projecting fence at all sides with putty or other suitable material, so that the liquid can cover to a depth of from one-eighth to a quarter of an inch the whole surface of the glass which is to be silvered. The surface of the glass should be clean and polished before pouring on the liquor above described, and when the liquor has been run on to the surface of the glass a few drops, say, from six to twelve, of a mixture consisting of one part by measure of oil of cloves to three parts of spirits of wine, are to be dropped at different places into the liquor on the glass, such six to twelve drops of diluted oil of cloves being the proper quantity for the quantity of liquor above mentioned, or the oil of cloves may be mixed with the liquor just before bringing the same in contact with the glass to be silvered. It should be stated that the more oil of cloves used the more quickly does the deposit of silver take place, but I prefer that the process of precipitation or deposition should take about two hours. . . . I have found that the use of a small quantity of oil of thyme or of carraways varies the colour of the silver, and will be useful in some cases for that purpose. . . . As far as my experience goes, I have found that about 18 grains of nitrate of silver are used for each square foot of glass. . . . As soon as the silver on the glass is perfectly dry, I varnish the back of the silver, and I prefer for such purpose beeswax and tallow in about equal quantities melted together.

"Having thus described the nature of the invention and the means pursued by me in performing the same, I further say that I do not confine myself to the precise details herein described, provided the peculiar character of the invention be retained whereby silver is deposited on to glass from a solution of that metal by deoxidation in such a manner as to cause the silver to adhere to glass without any previous coating of the latter."

This invention of Drayton attracted immediate attention. At a meeting of the Chemical Society held on April 15th, 1844, Robert Warington, who was at that time Secretary, described the process (*Memoirs and Proc. Chem. Soc.*, 1844, ii., 128), and showed a mirror made by it, which evidently impressed the audience, for the admiration excited is mentioned in a rather full account of the meeting given in *Dingler's Polytechnisches Journal* (1884, xcii., 472).

Faraday also lectured upon it at the Royal Institution, and the *Athenæum* of June 15th, 1844, in giving an account of the lecture, which was entitled "On Recent Improvements in the Manufacture and Silvering of Mirrors," says:—"The great subject of the evening was the invention of Mr. Drayton, which entirely dispenses with mercury and tin. By that gentleman's process the mirror is for the first time, literally speaking, 'silvered,' inasmuch as silver is precipitated on it from its nitrate in the form of a brilliant lamina." After describing the method it adds:—"This part of Mr. Faraday's discourse was illustrated by three striking adaptations of Mr. Drayton's process. He (Faraday) first silvered a glass plate the surface of which was cut in a ray-like pattern, then, secondly, a bottle was filled with Mr. Drayton's transparent solution, which afterwards exhibited a cylindrical reflecting surface, and finally a large cell made of two glass plates was placed erect on the table and filled with the same clear solution. This, although perfectly translucent in the first instance, gradually became opaque and reflecting, so that before Mr. Faraday concluded those of his auditors who were placed within view of it saw their own faces, or those of their neighbours, gradually substituted for the faces of those who were seated opposite to them."

Although the mirrors manufactured by Drayton's ingenious device were very beautiful, they never came into actual use, as it was found that they were liable, in the course of a few weeks, to become dotted over with small brownish red spots, which greatly spoiled their appearance.

These spots are due, according to Stenhouse (*Mem. and Proc. Chem. Soc.*, 1844, ii., 242; *Annalen*, 1845, liv., 102), to the fact that the metallic silver, while being deposited on the surface of the glass, carries down with it mechanically small quantities of resinous matter, resulting most probably from the oxidation of the essential oil. In the course of time this resinous matter, which is interposed between the glass and the silver, begins to act on the metallic surface with which it is in contact, and produces small brown spots. Stenhouse noted that if an excess of oil of cloves was employed the flecks appeared much sooner.

This circumstance caused Drayton to modify his process, and in 1848 he took out another patent. The specification (A.D. 1848, No. 12,358) reads:—"My invention consists in causing silver to be deposited on to glass from a solution of silver in such a manner that a precipitate of silver will adhere to the glass without any previous coating being applied, and in order that the invention may be fully understood I will describe the means pursued. I take one ounce of hartshorn, or ammonia, and two ounces of nitrate of silver, three ounces of water, and three of spirit (I prefer spirits of wine), mixing these carefully together. I allow the liquid to stand three or four hours, and then filter it for use. To one ounce of the filtered fluid I add a quarter of an ounce of saccharine matter dissolved in equal parts (say, about half a pint of each) of spirit and water; I prefer grape-sugar so dissolved if the solution is allowed to stand a few hours. The invention is applicable for the manufacture of looking-glasses and every other description of glass, either hollow or with a flat surface, that it is desirable to coat with silver. There is nothing at all unhealthy or injurious in the method thus employed, and no smell of any kind arises from it either during the process or after the glass is silvered. It can be employed either in a horizontal or vertical position, provided the liquid be kept in contact with the surface of the glass intended to be silvered, the glass being kept heated to about 160° F. during the process. As soon as the silver on the glass is perfectly dry it may be varnished with common mastic varnish, which preserves it thoroughly from friction.

"The superiority of this invention over all others yet known consists in its perfect durability, and its withstanding heat to a very extraordinary extent, as well as damp, which renders it equally serviceable in all climates. This solution will deposit silver upon metals in a very perfect manner."

This new method also appears not to have given satisfactory results, for patents were subsequently taken out protecting the use of various reducing agents; these, however, introduced no new principle, nor were they real improvements upon Drayton's procedure.

Among others, in 1855, Hill (Specification, A.D. 1855, 1093) protected a process for silvering glass in which invert sugar was used as the reducing agent (he recommends a temperature of 212° F. for the deposition); later in the same year, Petitjean took out a patent (Specification, A.D. 1855, 1681) in which tartaric acid was employed at a temperature of 150° F.

It must not be overlooked that the difficulties originally met with in manufacturing silver-coated mirrors on a large scale were not entirely due to defects in the silvering process, but also to defects in the glass used or in its polishing and subsequent treatment. It was only after many failures that mirror makers sufficiently recognised what apparently trifling details materially affected the results. For example, if plates of glass after polishing are allowed to remain in a case for some days during transit, separated by strips of paper or flannel, the places where the paper or flannel comes into contact with the glass are clearly distinguishable after silvering, the metal being noticeably duller there than upon the untouched portions.

No really satisfactory method of silvering glass was,

however, devised until Liebig took up the study of the process with the object of finding a liquid able to deposit, at the ordinary temperature, a permanent coherent film of silver which would not later develop spots. Liebig published his results in 1856 (*Annalen*, 1856, xcviii., 132). An important point of his work is that he was the first to notice and employ the effect of caustic alkali in accelerating the rate of reduction of silver. He recommended that the glass should be silvered face downwards in an ammonical solution of silver nitrate containing caustic soda mixed with an aqueous solution of milk-sugar.

To prepare Liebig's silvering solution, 1 grm. of silver nitrate is dissolved in 20 cc. of water, and just enough of a solution of ammonia added to dissolve the silver oxide at first thrown down. This liquid is mixed with 45 cc. of a solution of caustic soda of specific gravity 1·035, and the precipitate again produced, re-dissolved by more ammonia. To ensure the absence of any excess of the latter, which retards the reduction, enough of a dilute solution of silver nitrate is dropped in to produce a slight permanent precipitate. This solution is finally made up with water to 150 cc., and allowed to settle. Immediately before use the clear silvering solution is mixed with one-sixth of its volume of a 10 per cent aqueous solution of milk-sugar. The plate to be silvered is suspended with the face to be coated downwards, so that the glass surface everywhere touches the liquid, and is at least 1 cm. from the bottom of the vessel.

Reduction begins immediately the milk-sugar is added, and is ended in about a quarter of an hour at the ordinary temperature. If the solution is warmed, reduction is much more rapid, and is complete in a few minutes. After washing with distilled water and drying in a warm place, the silver adheres firmly to the glass, and with care can be polished to a perfect mirror. Liebig states than an estimation of the silver thus thrown down showed that 1 square metre of the film produced contained 2·21 grms. of silver.

Much later, Liebig recommended a somewhat different procedure (*Annalen*, 1867, Suppl. V., 257). The silver solution employed is prepared by adding caustic soda to an aqueous solution of silver nitrate containing ammonium sulphate. The reducing liquid is made by mixing two liquids, one a solution of cane-sugar inverted by boiling with tartaric acid, the other a solution of cupric tartrate in caustic soda. Liebig states that he is unable to explain the action of the copper, but that when it is used the silver is much more uniformly deposited and less liable to contain flecks and holes.

Either of Liebig's processes if properly carried out gives a perfectly satisfactory result, and his original process is still preferred by some persons.

Concave mirrors made by depositing silver on a polished glass surface received early an important application in reflecting telescopes. The mirrors used in such instruments were originally constructed of a hard white alloy of copper and tin containing a little arsenic known as speculum metal. Such mirrors had so many grave disadvantages that they have fallen out of general use. The alloy is extremely brittle, and thus liable to fracture, even a sudden change of temperature sometimes causing this; its great weight makes it difficult to mount, and it reflects about one-third less light than silver. Its greatest drawback, however, is its liability to tarnish, after which the mirror can only be again made fit for use by re-polishing and consequently re-figuring, which costs nearly as much as a new one.

The suggestion to use silvered glass in place of speculum metal was originally made by Foucault (*Comptes Rendus*, 1857, xliv., 339), who, apparently unaware of Liebig's recent work, employed films deposited by Drayton's method.

Draper employed such a silvered speculum in his large reflecting telescope, and describes in detail how he silvered it ("Smithsonian Contributions to Knowledge," 1865, xiv.). He, following Foucault, at first used Drayton's process, but like other observers, finding it to give mirrors liable to spot, abandoned it in favour of a modification of one patented by Cimeg in 1861 (Specification, A.D. 1861, No. 619), in which Rochelle salt is used as the reducing agent. Draper states that the thickness of the silver thus deposited is about one two-hundred thousandth of an inch, and that the metal deposited on a circular mirror 15½ inches in diameter weighs less than 4 grains.

The advantages of reflectors of silvered glass are well seen in Commons' 36-inch Newtonian telescope finished in 1879, and transferred in 1895 to the Lick Observatory, and in the 5-foot reflector constructed by him on a similar plan for the Harvard College Observatory in 1904.

Browning in his book ("A Plea for Reflectors," Sixth Edition, 1876), recommends Liebig's original process for silvering specula, and gives the following very full directions for carrying it out:—"Prepare three standard solutions: (A) Silver nitrate 90 grains dissolved in 4 ozs. of distilled water; (B) caustic potash (purified by dissolving in alcohol) 1 oz., dissolved in 25 ozs. of distilled water; (C) milk sugar in powder ½ oz., dissolved in 5 ozs. of distilled water. Of these solutions, A and B may be kept in stoppered bottles for any length of time, but C must be fresh. To prepare sufficient of the silvering fluid to coat an 8-inch speculum, pour 2 ozs. of Solution A into a glass vessel capable of holding 35 fluid ozs., drop in cautiously, stirring all the time with a glass rod, as much liquid ammonia as is just necessary to obtain a clear solution of the precipitate first thrown down, and add 4 ozs. of Solution B. The brownish black precipitate formed must be just re-dissolved by the addition of more ammonia as before. Dilute the liquid with distilled water until its bulk reaches 15 ozs., and drop in some of Solution A until a slight precipitate, which does not dissolve after stirring for three minutes, is obtained. Then dilute with 15 ozs. more of distilled water, and set the whole aside to settle. Do not filter. When all is ready for immersing the mirror add to this silvering solution 2 ozs. of Solution C, and stir gently and thoroughly. Solution C may, if necessary, be filtered."

(To be continued).

THE

EFFECT OF PRESSURE UPON ARC SPECTRA.*

No. I.—Iron.

By W. GEOFFREY DUFFIELD, B.Sc., B.A.

The first part of the paper contains a description of the mounting and adjustment of the large Rowland Concave Grating in the Physical Laboratory of the Manchester University. The feature of this is the stability of the carriages carrying the grating and camera, and the novel construction and attachment of the cross-beam, which secure the absence of any disturbance which might be caused by bending or sagging.

The second part describes experiments made with a pressure cylinder designed by Mr. J. E. Petavel, F.R.S., in which an arc is formed between metal poles opposite a glass window, through which the light is examined by means of the Grating Spectroscope. A system of mirrors allows the image of the arc, however unsteady it may be, to be kept almost continuously in focus upon the slit.

Two sets of photographs of the iron arc in air have been taken for pressures ranging from 1 to 101 atmospheres (absolute), and the results are given below for wave-lengths $\lambda = 4000$ A.U. to $\lambda = 4500$ A.U.

I. *Broadening.*

1. With increase of pressure all lines become broader.
2. The amount of broadening is different for different

* Abstract of a Paper received by the Royal Society, July 4, 1907.

lines, some almost becoming bands at high pressures, and others remaining comparatively sharp.

3. The broadening may be symmetrical or unsymmetrical; in the latter case the broadening is greater on the red side.

II. *Displacement.*

1. Under pressure the most intense portion of every line is displaced from the position it occupies at a pressure of 1 atmosphere.

2. Reversed as well as bright lines are displaced.

3. With increase of pressure the displacement is towards the red side of the spectrum.

4. The displacement is real and is not due to unsymmetrical broading.

5. The displacements are different for different lines.

6. The lines of the iron arc can be grouped into series according to the amounts of their displacements.

7. Three groups can in this way be distinguished from one another; the displacements of Groups I., II., III. bear to one another the approximate ratio 1 : 2 : 4. (The existence of a Fourth Group is suggested by the behaviour of two lines, but further evidence is needed upon this point; 1 : 2 : 4 : 8 would be the approximate relations existing between the four Groups).

8. Though all the lines examined, with two possible exceptions, fall into one or other of these Groups, the lines belonging to any one Group differ to an appreciable extent among themselves in the amounts of their displacements.

9. The relation between the pressure and the displacement is, in general, a linear one, but some photographs taken at 15, 20, and 25 atmospheres pressure give readings incompatible with this relation, Other photographs at 15 and 25 atmospheres present values which are compatible with it.

10. The abnormal readings are approximately twice those required by the displacements at other pressures, if the displacement is to be a continuous and linear function of the pressure throughout.

11. On the photographs showing abnormal displacements the reversals are more numerous and broader than they are on plates giving normal values, and there is some evidence in favour of a connection between the occurrence of abnormal displacements and the tendency of the lines to reverse.

III. *Reversal.*

1. As the pressure is increased, reversals at first become more numerous and broader.

2. The tendency of the lines to reverse reaches a maximum in the neighbourhood of 20 to 25 atmospheres, and a further increase in pressure reduces their number and width.

3. Two types of reversal appear on the photographs, symmetrical and unsymmetrical.

4. Within the range of pressure investigated, the reversals show no tendency to change their type.

5. In the case of unsymmetrically reversed lines in the electric arc, the reversed portion does not, in general, correspond to the most intense part of the emission line, being usually on its more refrangible side.

6. The displacements of the reversed parts of the unsymmetrically reversed lines of Group III. are about one-half the displacements of the corresponding emission lines. Indeed, the reversed parts of the lines of Group III. fall approximately in Group II.

7. No relation between the order of reversal and the frequency of vibration, such as exists in the spark, has been observed in the iron arc for the ranges of wave-length and pressure examined.

IV. *Intensity.*

1. The intensity of the light emitted by the iron arc is, under high pressures, much greater than at normal atmospheric pressure.

2. Changes in relative intensity of the lines are produced by pressure. Lists of enhanced and weakened lines are given.

THE TITRATION OF MERCUROUS SALTS WITH POTASSIUM PERMANGANATE.

By D. L. RANDALL.

If a solution of a mercurous salt, such as mercurous sulphate in dilute sulphuric acid, is titrated with potassium permanganate in the usual manner, the bleaching of the colour is rapid at first, but long before the oxidation is complete the solution assumes a golden-yellow colour, and on standing the brown oxides of manganese are precipitated. For this reason no definite end-reaction is obtainable. This difficulty is, however, avoided if the permanganate solution is added in excess, the colour then bleached with a standard ferrous sulphate solution, and the end-point finally reached by a few drops of permanganate. Under these conditions the end-reaction is perfectly sharp and the oxidation of the mercurous salt complete, as may be proved by adding hydrochloric acid to the solution.

In the preliminary experiments this process was tested upon weighed portions of commercial chemically pure mercurous sulphate, which was dissolved in dilute sulphuric acid. So much difficulty was experienced in dissolving the salt in quantities suitable for experiment that recourse was taken to the very doubtful procedure of heating the liquid (boiling or prolonged heating on the steam-bath) to hasten the solution. Although the end-reaction was in every case as sharp as could be desired, and the oxidation complete, the results were low and variable, indicating from 90 to 93 per cent of mercurous sulphate in the sample used. This was probably due to the partial oxidation of the mercurous salt during the process of solution.

A few experiments in which the salt was dissolved in hot concentrated phosphoric acid, and the solution then diluted and titrated without further addition of acid, gave results much nearer the theory but still very variable.

For the final experiments a large quantity of a mercurous sulphate solution was prepared by shaking up an excess of the salt in water acidified with sulphuric acid, allowing the whole to stand for twenty-four hours, and finally filtering through asbestos. Portions of this solution for standardisation or titration were measured out in a 100 cc. burette or weighed out in a dry counterpoised beaker. The standard of this solution was obtained by precipitating the measured or weighed portions in the cold with a slight excess of sodium chloride. After twelve hours' standing, the precipitated mercurous chloride was collected upon asbestos in a platinum crucible and dried to a constant weight at the ordinary temperature in a vacuum desiccator over sulphuric acid. The method of drying in a vacuum is recommended by Hulett (*Zeit. Phys. Chem.*, 1904, xlix., 500) as much more trustworthy than the usual one of drying in the air-bath at 105—110° C., where there is danger of volatilisation—a statement which the experience of the present writer has fully borne out. (Hulett, however, employed calcium chloride instead of sulphuric acid as the drying agent; Treadwell, *Lehrbuch Anal. Chemie*, ii., 114, states that when the drying is carried out at 105° the results are always about 0·4 per cent too low). In every case the standard of the mercurous solution used was fixed by two or more gravimetric determinations made on the same day as the corresponding series of titrations.

The solutions of permanganate and of ferrous sulphate used were both approximately twentieth normal. The reason why it is desirable to use solutions more dilute than the usual tenth normal strength is obvious when we note that 0·1 cc. of the above twentieth normal permanganate is equivalent to about 1 mgrm. of mercury. For the same reason the titrations must be performed with all possible care and accuracy. All the burettes used in the present investigation had been standardised by the Berlin Reichsanstalt.

As the oxidation of mercurous salt by an excess of permanganate is very rapid, no great care is necessary in regulating the amount of the excess. It is sufficient in

TABLE I.

Hg_2SO_4 solution. Cc.	Dilution at titration. Cc.	H_2SO_4 (1 : 1). Cc.	$KMnO_4$ approx. N/20. Cc.	$FeSO_4 = KMnO_4$. Cc.	$KMnO_4$ final. Cc.	Hg found. Grm.	Hg theory. Grm.	Error. Grm.
				A.				
100	150	5	14·70	10	10·90	3·80	0·0346	0·0354	−0·0008
100	150	5	14·72	10	10·90	3·82	0·0347	0·0354	−0·0007
100	150	5	14·70	10	10·90	3·80	0·0346	0·0354	−0·0008
100	150	5	14·71	10	10·90	3·81	0·0346	0·0354	−0·0008
				B.				
Grms.								
505·8	500	5	29·20	10	10·90	18·30	0·1668	0·1666	+0·0002
500·2	500	5	32·16	13	14·17	17·99	0·1639	0·1648	−0·0009
510·1	500	5	29·29	10	10·90	18·39	0·1676	0·1680	−0·0004
499·2	500	5	28·95	10	10·90	18·05	0·1645	0·1644	+0·0001

TABLE II.

$FeSO_4$. Cc.	Dilution. Cc.	H_2SO_4 (1 : 1). Cc.	HNO_3. Cc.	Approx. N/10 $KMnO_4$. Cc.
25	200	5	0	13·37
25	200	5	0	13·39
25	200	5	0	13·41
25	200	5	0	13·38
25	200	5	0	13·38
25	200	0	3	13·38
25	200	0	5	13·40
25	200	0	5	13·41
25	200	0	5	13·40
25	200	0	5	13·38
25 (*a*)	200	5	0	13·47
25	200	5	0	13·50
25	200	5	0	13·49
25	200	0	5	13·53
25	200	0	10	13·50
25	200	0	20	13·51
20	200	0	30	13·00

(*a*) Changed $FeSO_4$ solution.

TABLE III.

$Hg_2(NO_3)_2$ solution. Cc.	Dilution. Cc.	HNO_3. Cc.	Approx. N/20 $KMnO_4$. Cc.	$FeSO_4 = KMnO_4$. Cc.	$KMnO_4$ final. Cc.	Hg found. Grm.	Hg theory. Grm.	Error. Grm.
25	200	5	49·99	9·76	10·64	39·35	0·3586	0·3594	−0·0008
25	200	5	49·68	9·50	10·36	39·32	0·3583	0·3594	−0·0011
25	200	5	49·73	9·50	10·36	39·37	0·3588	0·3594	−0·0006
25	200	5	49·89	9·67	10·54	39·35	0·3586	0·3594	−0·0008
25	200	5	49·70	9·50	10·36	39·34	0·3585	0·3594	−0·0009
		H_2SO_4 (1 : 1).						
25	200	5	50·29	10·00	10·90	39·39	0·3589	0·3594	−0·0005

practice to continue the addition of permanganate until the solution, coloured brown by the oxides of manganese, takes on a distinctly red tint. Under these circumstances the ferrous sulphate can be added immediately, and the titration completed. Table I. gives the results obtained with mercurous sulphate.

For practical purposes the application of the method to mercurous nitrate is of much greater importance. In Schneider's method for the determination of manganese (*Ding. Pol. Journ.*, cclxix., 224), permanganic acid is titrated with hydrogen peroxide in the presence of nitric acid. Ibbotson and Brearley (CHEMICAL NEWS, lxxxiv., 247) in their modification of this process recommend the use of standard ferrous ammonium sulphate instead of hydrogen peroxide. Blair also studied this process, and recommends the use of ferrous ammonium sulphate (*Journ. Am. Chem. Soc.*, xxvi., 793; also "Chemical Analysis of Iron," Sixth Edition, p. 121). In the absence of any data concerning the quantity of nitric acid that can safely be present in the titrations of ferrous sulphate the determinations in Table II. were made. The nitric acid used was rendered free from the lower oxides of nitrogen by the prolonged passage of a current of air. The acid used in all the subsequent experiments was purified in a similar manner.

When more than 10 per cent by volume (20 cc. in 200 cc.) of the concentrated acid was present, the oxidation of the ferrous salt by the nitric acid was evident in the change of colour of the solution, low results, and uncertain end reaction.

(NOTE.—As nitrous acid is at least in part oxidised by direct titration with potassium permanganate, and completely when an excess is used—method of Kinnecut and Nef, *Am. Chem. Journ.*, v., 388—only a part of the loss due to oxidation of the ferrous salt by the nitrous acid would appear in the result).

This table shows that when the titration is made without unnecessary delay after adding the acid, as was the case here, 3 per cent of pure nitric acid, the amount used in the subsequent experiments, has no appreciable effect on the estimation of ferrous iron.

In Table III. are given the results of a series of determinations of mercurous nitrate by the method described above. A solution was prepared by dissolving the crystallised salt in water containing enough pure nitric acid to prevent the formation of basic salts. As an additional precaution a current of hydrogen, washed by alkaline permanganate and alkaline pyrogallol, was passed for twelve hours through the solution to remove nitrous acid. Measured portions of this solution, which was standardised

gravimetrically as given above, were diluted to 200 cc., further acidified with pure nitric acid, and titrated in the manner already described.

In the last experiment sulphuric acid was added instead of nitric acid, yet, as the table indicates, without apparent effect on the result.

This investigation has shown :—

1. That mercurous sulphate and mercurous nitrate can be readily estimated by potassium permanganate with a very fair degree of accuracy.

2. That ferrous salts can be successfully titrated in the presence of at least 3 per cent of nitric acid.

In closing, the writer gratefully acknowledges the suggestions of Dr. R. G. Van Name which led to this investigation.—*American Journal of Science*, xxiii., p. 137.

A REVISION OF THE ATOMIC WEIGHT OF POTASSIUM.*

II. The Analysis of Potassic Bromide.

By THEODORE WM. RICHARDS and EDWARD MUELLER.

Introduction.

The foregoing quantitative study of potassic chloride by Dr. Arthur Staehler and one of the present authors affords strong evidence that the atomic weight of potassium is about 39·114, slightly lower than the value based upon the work of Stas. The authors fully appreciated, however, that the investigation of a single compound is not enough to establish a chemical constant so important as this, and, accordingly, the present investigation was prosecuted simultaneously. It was expected that the two investigations might either support one another, or else, by affording incompatible results, lead to the discovery of a constant error in one or the other, and thus pave the way for further advance in knowledge. As will be seen, the work on the chloride was satisfactorily confirmed by the work on the bromide.

In the present case the careful study of potassic bromide was particularly necessary, because there already exist two concordant series of experiments upon this substance, performed by the old masters, Marignac and Stas, pointing to a value in the neighbourhood of 39·14, instead of the before-mentioned new value 39·11. In this case the higher value for potassium is not diminished, as in the case of the chloride, by an additive correction in the atomic weight of the halogen, because Baxter has shown Stas's estimate for bromine to have been nearly correct. Hence, the discrepancy remains one too serious to be tolerated.

(A brief review of Stas's and Marignac's work may be found in Clarke's "Re-calculations," 1897, p. 47. Baxter's work is to be found in *Proc. Am. Acad.*, 1906, xlii., 201; *Journ. Am. Chem. Soc.*, 1906, xxviii., 1322. See also Richards, *Trans. Am. Phil. Soc.*, 1904, xliii., 116).

The careful study of this work of Stas and Marignac affords convincing evidence that the potassic bromide used by them for analysis was not sufficiently pure for the purpose. Stas admitted that some of his preparations were not even wholly soluble in water, and his method of procedure was such that some of them probably contained platinum and hydroxide. Because speculations of this kind concerning work so long past are of but little value, it was clearly necessary to repeat this work with modern care, and the following pages recount the details of the repetition.

In common with others of the same type, the investigation easily resolves itself into several sections, and will be discussed under the following heads :—The preparation of materials, the drying and weighing of potassic bromide, the determination of the ratio of argentic to potassic bromide; the determination of the ratio of silver to potassic bromide, and the discussion of the results. Of the laboratory tasks the preparation of the materials was by far the most laborious and puzzling, while the analytical work was comparatively simple.

The Preparation of Materials.

The Source of the Potassium.—The task of preparing pure potassic bromide, simple as it may appear, is by no means an easy one. In view of our experience, it seems probable that neither Marignac nor Stas ever prepared samples pure enough to correspond with the other precautions which they took. As in the case of sodic bromide, the salt itself when once made cannot be effectively purified (Richards and Wells, *Proc. Am. Acad.*, 1906, xli., 435; *Zeit. Phys. Chem.*, 1906, lvi., 348). In this respect it differs widely from the chloride. We found after due trial that the potassium and bromine must be purified separately in such forms as to introduce no foreign matter. Accordingly, the two substances, already adequately purified, were caused afterwards to yield potassic bromide; and this salt, when re-crystallised, gave the final substance for analysis. The purification of the potassium materials will be discussed first.

It was necessary to provide potassium material which should be free from the suspicion of introducing any impurity with the metal desired, either basic or acid. Potassic nitrate, which had served so well in the case of the chloride, was not suitable for the present purpose, because the destruction of the nitric acid involves too great a sacrifice of laboriously prepared hydrobromic acid. After due consideration, potassic oxalate was tentatively chosen. It was necessary to prove that this salt can be easily and certainly purified by re-crystallisation, and especially to show that the other alkali metals can thus be separated. The following tests accomplish this proof :—

A saturated solution of potassic oxalate containing a purposely added admixture of 10 per cent of sodic oxalate was crystallised, and the crystals drained centrifugally. By the flame test, a pronounced difference was noticeable between the amount of sodium present in the mother-liquor and that in the crystals. A second re-crystallisation and whirling was still more satisfactory; the crystals gave no sodium test to the eye, while the mother-liquors gave a distinct yellow. This indicates that sodium has a decided tendency into the mother-liquors, and hence can be separated by fractional crystallisation.

Again, 1 per cent of lithium salt was added to potassic oxalate with similar outcome. Rubidium and cæsium were tested likewise. A saturated solution of potassic oxalate and a salt of each of these metals was made of such strength that the rubidium or cæsium could easily be found by means of the spectroscope. Each solution was evaporated until saturated, and cooled; and the crystals were whirled. The mother-liquor gave a test for the impurity, the crystals gave none.

No other oxalates were seriously to be feared, because the insoluble ones would appear at once and demand filtration, and soluble double oxalates could hardly be isomorphous, and would therefore tend into the mother-liquors. Traces of calcic oxalate in fact appeared in the former fashion, and traces of iron in the latter.

In view of these satisfactory results, it was evidently only necessary to crystallise the potassic oxalate often enough to make the separation complete; and since potassic oxalate has a fairly convenient change in solubility with the temperature, the yield after a considerable number of crystallisations is good, especially if pains are taken to carry out the process systematically.

Two very pure samples of oxalate were made, from two different sources. As one source of material, a commercial sample prepared by Merck was used. It had been labelled "Potassium oxalate, neutral, highest purity," and contained, as a matter of fact, only the traces of calcium and iron already referred to, but no lead or other discoverable impurity. A large quantity of a solution of this salt was filtered hot into a platinum dish, where it was five times systematically re-crystallised, the crystals being centrifugally whirled each time.

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Careful scrutiny in the spectroscope revealed in the product no other spectroscopic lines than those of potassium, and careful qualitative tests proved the absence of lead and iron. The salt dissolved without a trace of residue in water, and was quite pure enough to serve as a starting point for further operations, to be described under the heading "Potassic Bromide."

A second sample of potassic material was obtained from Merck in the form of the hydroxide, being marked "Potassium Hydrate, Chemically pure Reagent; conforms to the standards of Dr. Krauch." It was, in fact, very pure, giving a perfectly clear solution both before and after neutralisation. It was neutralised with a specimen of oxalic acid which had been carefully purified by Mr. G. E. Behr, jun., for other work. This acid contained no halogens, and left no residue on volatilisation in platinum. Slightly more than the equivalent quantity of acid was added, and the oxalate obtained was therefore slightly acid. As will be shown, the acidity was later the cause of much inconvenience, and had better have been avoided. The oxalate was four times systematically re-crystallised in platinum with centrifugal draining each time. The final product, like the previous one, gave no tests for impurities except a slight excess of acid; it was used as the source of potassium for one preparation of potassium bromide.

Bromine.—Although the methods previously used at Harvard had afforded a satisfactory yield of very pure bromine, it was desired to add to the knowledge on the subject by testing another method (see *Proc. Am. Phil. Soc.*, 1904, xliii., 119; for references, and Stas, *Mém. Acad. Belgique*, 1882, xliii., II., 38). Through the generosity of the Mallinckrodt Chemical Works of St. Louis, Missouri, and also of the Dow Chemical Works of Midland, Michigan, a large quantity of potassic bromate was placed at our disposal. Repeated crystallisation, very kindly carried out for us on a large scale by these firms, had been the method used in its purification.

This material, which served as our starting-point, was already very pure, a fact which was indicated by three syntheses of argentic bromide from purest silver and potassic bromide obtained by decomposing the Mallinckrodt bromate. These syntheses, carried out with all necessary precautions, gave, respectively, 57·441, 57·440, 57·441 as the percentage of silver in argentic bromide. According to Baxter the true amount is 57·445 (Baxter, *Journ. Am. Chem. Soc.*, 1906, xxviii., 1332; see also Richards, *Trans. Am. Phil. Soc.*, 1904, xliii., 119). The slight difference indicates a trace of iodine rather than chlorine; but this impurity can be easily expelled, while chlorine is far more troublesome.

It having been demonstrated that re-crystallisation is an effective means of purifying the salt from chlorate and chloride, a large quantity of potassic bromate was three times re-crystallised in porcelain, the crystals being centrifugally whirled each time and all mother-liquors discarded. This gave an exceedingly pure bromate, much purer than Stas could have obtained ("Untersuchungen," 160), because the centrifugal draining makes so great a difference in the rate of purification (Richards, *Journ. Am. Chem. Soc.*, 1905, xxvii., 104).

A large quantity of the salt was decomposed into the bromide in a platinum dish by the heat of an alcohol lamp. The potassic bromate in decomposing attacked the platinum, and the mass of bromide was slightly brownish in colour, but this caused no inconvenience in the present case, as the bromine was to be subsequently distilled. In order to liberate the halogen, the bromide was treated in strong solution with less than the calculated quantity of bromate and an excess of pure sulphuric acid. The acid was added drop by drop to the mixed solution of salts in an apparatus made entirely of Jena glass, which was kept surrounded by ice-water. The bromine which volatilised on account of the heat of the reaction was caught in a condenser under water; to this was added the remaining bromine, which had been separated from the supernatant solution by means of a separating funnel.

The bromine thus obtained was twice distilled by steam heat into water in a Jena glass condenser, packed in ice. It was kept in a well-seasoned bottle with double ground-glass stoppers.

The product was certainly free from non-volatile materials, and could have contained only iodine, and, perhaps, a trace of sulphuric acid as impurity. It will be seen that these were eliminated in the subsequent work. This was the only sample of bromine prepared; it was used in all the preparations of bromide, as the quantitative results indicated that it was very pure.

Potassic Bromide.—The problem of obtaining potassic bromide from the oxalate and bromine had been carefully considered before these substances had been prepared. Only two methods recommended themselves for the present purpose, although the bromide can be obtained from these two materials by a variety of reactions, which would ordinarily be acceptable. Here, however, simplicity, completeness, and theoretical correctness must all be fulfilled; that the methods adopted really possessed these advantages in their favour must be admitted after careful perusal of the following description of the details.

In some preliminary experiments it was shown that by adding an excess of bromine to the oxalate and evaporating off the excess, a very pure bromide quite free from oxalate is obtained. Accordingly, a quantity of the first sample of five times crystallised potassic oxalate was treated with an excess of bromine, the bromine being added in small quantities from a dropping-funnel. The solution was held in a quartz dish, which was carefully hooded to prevent entrance of dust. When the action had ceased, the solution was heated on a steam-bath until any traces of iodine and all excess of bromine had been expelled. The solution was found to be entirely free from oxalic acid upon testing with calcic nitrate in a solution faintly acid with nitric acid. Although it was wholly colourless while in the quartz dish, after being concentrated in platinum it developed a very faint yellow tinge. Upon re-crystallising three times this colour was finally concentrated in the extreme mother-liquor, and was found to be due to a trace of platinum; no iron was present. Even the first crystals were perfectly white, the second and third mother-liquors also showed no trace of colour, and only the first of the mother-liquors gave a test for platinum.

The material thus prepared, after being three times re-crystallised in platinum with centrifugal draining, was called Sample I., and served for Analyses 1 to 11.

The second sample of potassic bromide was prepared from the second sample of four times re-crystallised potassic oxalate. The method was the same as with the previous sample. An excess of bromine was added to the oxalate in quartz; when action ceased, the bromine was driven off by heating on steam-bath. However, on testing for oxalate, a perceptible quantity was found still undecomposed. This was unexpected, in view of the fact that the first preparation of bromide had given no trouble in this respect. The difficulty was traced to the presence of a small percentage of acid salt in the oxalate; the presence of acid has an inhibitory effect on the reaction of bromine on the oxalate ion. Obviously, the simplest remedy would have been to add pure potassic hydroxide; but this was not added because at that moment there was none at hand. Moreover, because the reaction was being performed in quartz, it was thought best not to use a caustic alkali for fear that the dish might be slightly attacked. The addition of a small amount of very pure re-crystallised bromate to this slightly acid solution served better, because its use was unattended with danger. Its employment was entirely effective; the ionised hydrogen was removed, and after adding more bromine and heating, a solution of bromide was obtained which contained no trace of oxalate.

This specimen was re-crystallised entirely in quartz, in order to prevent a recurrence of the trouble experienced with Sample I., as well as to see if the variation of conditions, affected the atomic weight. Two crystallisations

were made with centrifugal draining, and every precaution; and there was obtained finally a very pure colourless product, with which were made two analyses, Nos. 12 and 13. That a uniformly pure material had been made is shown by the close agreement of these two analyses with the mean of all.

As a further precaution against accidental error, it was thought best to develope a method essentially different from that just discussed, and to prepare therewith a third specimen of bromide. In brief, this method consisted in the separate preparation of pure ammonic bromide and potassic hydroxide, and the production of potassic bromide by the evaporation of the mixed solutions of these substances. Thus can be obtained a salt contaminated only with excess of volatile ammonic bromide.

The preparation of pure ammonic bromide was very easy. Ammonia essentially free from carbon compounds was redistilled into water in a platinum dish. Into this was dropped the purest bromine, which fell through the liquid into a small porcelain crucible resting on the bottom of the dish. In this way the bromine itself could not come into contact with platinum and attack it. The reaction took place very rapidly, yielding ammonic bromide which could have contained no non-volatile ingredients, because all its constituents had just been distilled.

The preparation of pure potassic hydroxide was less easy to devise, because more original; but the execution was almost as easy. The problem was solved by the use of an electrolytic process which will be described in greater detail elsewhere. In brief, a saturated solution of potassic oxalate (Sample I.) was electrolysed between a pure mercury cathode and a platinum anode in a porcelain dish cooled with ice, the current from four storage cells being used. When the amalgam became solid, the current was stopped, the solution decanted, and the amalgam washed, being triturated with an agate pestle under water, till no test for oxalate could be obtained. The pure amalgam was transferred to a platinum dish, covered with water, and made the anode of a dense current until only a little of the potassium amalgam remained undecomposed. Thus pure potassic hydroxide was formed. This solution was poured into the ammonic bromide solution, the mixture was evaporated and crystallised, and the salt thus obtained used for Analyses 14, 15, and 16.

The bromide thus obtained must have been very pure. During the electrolysis, the high concentration of the potassic oxalate (see Bunge, *Berichte*, 1876, ix., 78) would tend to allow the deposition of potassium only (Berthelot, *Ann. Chim. Phys.*, 1879, [5], xviii., 433). At any rate, metals less easy to deionise could hardly have been set free. During the later decomposition of water by the amalgam, all metals with less tendency to ionise would have remained in the mercury, because some of the amalgam was left undecomposed. Any trace of iodine which the bromine may have contained must have been driven off by the fusion just before analysis, this fusion being prolonged in order to expel ammonic bromide. The results of the analyses of this sample indicate its essential identity with the two preceding preparations. Since there was no known source of impurity in any one of the preparations, this was not surprising.

Although our consistent employment of insoluble vessels rendered the presence of colloidal silica unlikely, an effort was made to test for this impurity of sample II. by volatilising 3 grms. of it in a stream of nitrogen. Unfortunately, the high temperature of the electric furnace caused the platinum boat containing the salt to weld to the foil which surrounded it in the tube, so that no certain quantitative evidence could be obtained. Two minute black spots were visible in the boat; nothing else could be seen upon very careful scrutiny. If there were any silica present, the amount must have been too small to have had any appreciable influence on the final atomic weights. Time and material were lacking, hence the experiment was not repeated.

Silver.—The essential details of the preparation of pure silver, as developed by Richards and Wells, were followed in detail, and the reader is referred to their paper, as well as to the preceding paper of Richards and Staehler, for the particulars. Two samples of silver were made; they were found to be identical in quantitative behaviour.

The source of the material used for the first preparation was the pure precipitated argentic chloride remaining from the work of Richards and Wells on sodium. It was reduced to metallic silver with invert sugar in a strong solution of sodic hydroxide. The silver thus obtained was washed free from soluble matter and dissolved in nitric acid; the argentic nitrate after crystallisation and whirling was reduced with ammonic formate, yielding a beautiful crystalline mass of metal.

This pure silver, after very thorough washing, was fused on lime by means of a blast lamp whose tip had been carefully cleaned. The buttons which were thus obtained were cooled in the reducing-flame, washed free from lime, scrubbed with cleaned sea-sand, etched with strong nitric acid, and washed with the purest water, to serve as anodes in the electrolytic purification which was the next step. The electrolysis was carried on as already described in previous similar Harvard researches, and every step of the subsequent work may be found in detail in the preceding papers on sodic and potassic chloride (see *Proc. Am. Acad.*, 1903, xxxviii., 450; Richards and Wells, *Journ. Am. Chem. Soc.*, 1905, xxvii., 473; Richards and Staehler, *Publication* 69, Carnegie Institution of Washington; CHEMICAL NEWS, xcvi., p. 133). The metal was finally fused as usual on a boat of the purest lime in an atmosphere of hydrogen under a tension of 50 mm. The larger pieces, after etching with nitric acid, were cut into smaller ones of convenient size with a clean cold-chisel. They were again etched in order to dissolve all traces of iron, scrubbed with clean sand, washed with a jet of water, and etched yet again with acid, paying particular attention to the cut edges. (Richards and Archibald, *Proc. Amer. Acad.*, 1903, xxxviii., 450; Baxter, *Journ. Am. Chem. Soc.*, 1906, xxviii., 1329). Finally the pieces were dried over an alcohol lamp and kept in a desiccator over potassic hydroxide for use.

This silver was used both in most of the titrations against potassic bromide and as the source of argentic nitrate used in the precipitation of argentic bromide to be weighed.

A second sample of silver, prepared from somewhat less pure initial material, was put through a more elaborate and exhaustive round of purification, which need not be detailed. The preparation included five crystallisations as nitrate and two successive precipitations as metal by formate. This silver was fused into buttons of a size suitable for immediate use without cutting. They were cleaned by etching and washing, dried, and preserved free from impurity as usual, and were used in analyses 7 and 9.

Nitric Acid.—For preliminary work, ordinary "chemically pure" nitric acid was distilled once, using a platinum condenser and Jena glass receiver, the first third of the acid being discarded. For the final analyses this re-distilled product, already very pure, was once again distilled, as before, the first third being rejected. This distillate gave no test with the nephelometer, after dilution.

Water.—As usual in such work, all the water used had been carefully purified by double distillation, once from a fairly strong solution of alkaline potassic permanganate, and then alone. The distillate was caught in Jena glass receiving flasks, which were provided with special adapters to prevent the access of dust. The first and last fractions were always rejected, only the middle portion being used. The connection of the Jena glass boiling-flask with the pure tin condenser was made without rubber or cork (Richards, *Proc. Amer. Acad.*, 1894, xxx., 380). Such water gave every evidence of sufficient purity, as has been frequently pointed out.

The Laboratory.—A very essential precaution in every stage of this work was to effectually exclude hydrochloric acid. Accordingly, all the preparations of the bromide

were carried out in a private laboratory, used especially and only for this work, and wholly free from the interference caused by large classes or other researches. Great care was taken not to allow any hydrochloric acid in the room; indeed, not a drop was used there during the entire research. A separate ventilating fan prevented fumes from other laboratories from interfering with the work.

Utensils.—As usual, great care was taken to avoid the use of any vessels which under the given conditions might be attacked and thus pollute the substance in hand. When glass and porcelain were not harmful, as in the early stages of the preparation of silver, such receptacles were employed; but in the purification of the substance for analysis, platinum and quartz were always used.

(To be continued).

THE

APPLICATIONS OF GRIGNARD'S REACTION.*

By ALEX. McKENZIE, M.A., D.Sc., Ph.D.

(Continued from p. 145).

Section I. (*continued*).

Hydrocarbons.

(*a*) *Unsaturated Hydrocarbons.*—When the Grignard reaction is applied to aldehydes, ketones, &c., sometimes an unsaturated hydrocarbon is obtained instead of an alcohol. It is, in fact, often possible to select the experimental conditions so that either an alcohol or the unsaturated hydrocarbon, obtained from it by the elimination of water, is the product of the action; for example, Grignard obtains phenyldimethylcarbinol, $C_6H_5.C(OH)(CH_3)_2$, from magnesium methyl iodide (1 mol.) and acetophenone (1 mol.) (*Comptes Rendus*, 1900, cxxx., 1322; compare W. H. Perkin, jun., and Pickles, *Trans. Chem. Soc.*, 1905, lxxxvii., 671). If, however, magnesium methyl iodide (2 mols.) is added to acetophenone (1 mol.), the ether expelled, and the residue heated for six hours at 100°, the unsaturated hydrocarbon, metho-(1')-vinylbenzene, $\begin{matrix}C_6H_5\\CH_3\end{matrix}\!>\!C\!:\!CH_2$, results (Klages, *Ber.*, 1902, xxxv., 2633). Similarly, it is possible to prepare from mesityl oxide, $\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!C\!:\!CH.CO.CH_3$, either the hydrocarbon, $\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!C\!:\!CH.C\!<\!\begin{matrix}CH_3\\CH_2\end{matrix}$ (Grignard, *Comptes Rendus*, 1900, cxxx., 1324), or the alcohol, $\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!C\!:\!CH.C(OH)(CH_3)_2$ (Fellenberg, *Ber.*, 1904, xxxvii., 3578). To quote a third example, Kay and Perkin (*Trans. Chem. Soc.*, 1906, lxxxix., 839; compare also *Ibid.*, 1905, lxxxvii., 1100), starting with optically active ethyl Δ'-tetrahydro-*p*-toluate, $CH_3.CH\!<\!\begin{matrix}CH_2.CH\\CH_2.CH_2\end{matrix}\!>\!C.COOC_2H_5$, obtain, by the action of magnesium methyl iodide, optically active Δ^8-*p*-menthenol (8), $CH_3.CH\!<\!\begin{matrix}CH_2.CH\\CH_2.CH_2\end{matrix}\!>\!C.C(OH)(CH_3)_2$. When the latter compound, however, is simply left in contact with an ethereal solution of magnesium methyl iodide at the ordinary temperature, it is converted into the corresponding optically active unsaturated hydrocarbon, $\Delta^{3.8(9)}$-*p*-menthadiene, $CH_3.CH\!<\!\begin{matrix}CH_2.CH\\CH_2.CH_2\end{matrix}\!>\!C.C\!<\!\begin{matrix}CH_3\\CH_2\end{matrix}$.

In many cases only unsaturated hydrocarbons can be obtained, and not the corresponding tertiary alcohols, if it so happens that the latter are very unstable. Klages, in particular, prepared a large number of unsaturated 1'-alkylated styrenes, of which an example has already been quoted, namely, metho-(1')-vinylbenzene. When this hydrocarbon is reduced, it is converted into *iso*propylbenzene, $C_6H_5.CH(CH_3)_2$, with great ease. This method in the hands of Klages has proved highly useful for making a large number of saturated benzenoid hydrocarbons, which are difficult to prepare by other methods.

Various stilbene derivatives have been studied by F. and L. Sachs (*Ber.*, 1905, xxxviii., 511). Thus, *p*-dimethylaminobenzaldehyde, $(CH_3)_2N.C_6H_4.CHO$, with magnesium benzyl chloride gives the alcohol—

$$(CH_3)_2N.C_6H_4.CH(OH).CH_2C_6H_5,$$

and this, on distillation under diminished pressure, forms 4-dimethylaminostilbene, $(CH_3)_2N.C_6H_4.CH\!:\!CHC_6H_5$.

The same authors (*Ber.*, 1905, xxxviii., 517; compare Sachs and Michaelis, *Ber.*, 1906, xxxix., 2163) acted on *p*-dimethylaminobenzaldehyde with magnesium methyl iodide, and obtained methyl *p*-dimethylaminophenylcarbinol, $(CH_3)_2N.C_6H_4.CH(OH).CH_3$, from which, however, water was not eliminated in the manner expected. Klages's method of heating the reaction product with an excess of magnesium alkyl halide at 100° did not lead to the formation of dimethylaminostyrene as was anticipated, but N-dimethylcumidine was formed thus:—

$$(CH_3)_2N.C_6H_4.CH(OMgBr).CH_3 + CH_3MgBr = (CH_3)_2N.C_6H_4.CH(CH_3)_2 + MgO + MgBr_2.$$

The formation of hydrocarbons of the acetylene series by aid of the Grignard action has been imperfectly studied. According to Oddo (*Atti R. Accad. Lincei*, 1904, [5], xiii., 187), magnesium bromoacetylene, CH:CMgBr, is produced when a current of dry acetylene is passed into magnesium phenyl bromide, and from this derivatives of the acetylene series are obtained.

(*b*) *Saturated Hydrocarbons.*—Magnesium organic compounds are vigorously acted on by water with the production of hydrocarbons. This was one of the first observations which Grignard made with his reagents (*Ann. Chim. Phys.*, 1901, xxiv., 438; Tissier and Grignard, *Comptes Rendus*, 1901, cxxxii., 835). Methane, for example, is evolved by the addition of water to magnesium methyl iodide: $CH_3MgI + H_2O = CH_4 + MgIOH$.

An alcohol has the same effect as water. For example, $CH_3MgI + C_2H_5OH = CH_4 + OC_2H_5.MgI$.

Indeed, any compound containing a hydroxyl group behaves in this manner, this property of hydroxylic compounds having been recommended both as a means for their qualitative detection and for separating them from compounds which do not interact with the Grignard reagent (Tschugaeff, *Ber.*, 1902, xxxv., 3912). A method for the estimation of hydroxyl groups in carbon compounds is based by Hibbert and Sudborough on this reaction, where, however, amyl ether is substituted for ethyl ether in the preparation of the reagent (*Trans. Chem. Soc.*, 1904, lxxxv., 933). Zerewitinoff claims the method to be suitable for estimating the number of hydroxyl groups in a carbon compound (*Ber.*, 1907, xl., 2023).

Allotropic compounds generally act on the Grignard reagent in accordance with the hydroxylic structure; thus *l*-menthylacetoacetate reacts in accordance with the formula $CH_3.C(OH)\!:\!CH.COOC_{10}H_{19}$, and not as $CH_3.CO.CH_2.COOC_{10}H_{19}$ (McKenzie, *Trans. Chem. Soc.*, 1906, lxxxix., 380).

A regular current of methane is evolved by the addition of dry powdered ammonium chloride to magnesium methyl iodide (Houben, *Ber.*, 1905, xxxviii., 3017): $2CH_3MgI + NH_4Cl = 2CH_4 + NH_2.MgI + MgICl$. When a current of dry ammonia is passed into an ethereal solution of magnesium ethyl iodide, ethane is evolved: $C_2H_5MgI + NH_3 = C_2H_6 + NH_2.MgI$. Primary or secondary amines exhibit a similar behaviour. Thus with aniline and methyl aniline:—

$$C_2H_5MgI + C_6H_5.NH_2 = C_2H_6 + C_6H_5.NH.MgI,$$
$$C_2H_5MgI + C_6H_5.NHCH_3 = C_2H_6 + C_6H_5N(CH_3).MgI$$

(Meunier, *Comptes Rendus*, 1903, cxxxvi., 758; *Bull. Soc. Chim.*, 1903, xxix., 314).

The action of a primary amine is possibly, however,

* A Paper read before the British Association (Section B), Leicester Meeting, 1907.

more complex than this representation of Meunier, since Houben (*Ber.*, 1905, xxxviii., 3017) concludes that the action $2CH_3MgI + C_6H_5NH_2 = C_6H_5NH.MgI,CH_3MgI + CH_4$ takes place in the cold if the proportions of magnesium methyl iodide and aniline, indicated by the equation given, are used (compare Sudborough and Hibbert, *Proc. Chem. Soc.*, 1904, xx., 165). If, however, a second molecular proportion of aniline is added to the hot solution, methane is again evolved, thus :—

$$C_6H_5.NH.MgI,CH_3MgI + C_6H_5NH_2 = 2C_6H_5.NHMgI + CH_4.$$

A method for making aromatic hydrocarbons has been devised by Werner and Zilkens, who use the methyl sulphate (*Ber.*, 1903, xxxvi., 2116, 3618; compare Houben, *Ibid.*, 3083). Thus *p*-xylene in a 75 per cent yield is obtained from magnesium *p*-tolyl bromide :—

$$CH_3.C_6H_4.MgBr + (CH_3)S_2O_4 = C_6H_4(CH_3)_2 + CH_3.SO_4.MgBr.$$

Toluene is obtained from magnesium phenyl bromide in a similar manner.

In order to throw some light on the constitution of triphenylmethyl, Gomberg and Cone (*Ber.*, 1906, xxxix., 1461, 2957) prepared tetraphenylmethane by the interaction of magnesium phenyl bromide and triphenylchloromethane: $C_6H_5MgBr + (C_6H_5)_3CCl = (C_6H_5)_4C + MgClBr$.

The method renders possible the introduction of various radicals in place of the methane hydrogen atom in triphenylmethane; for example, the asymmetrical tetraphenylethane is readily formed by aid of magnesium benzyl chloride :—

$$C_6H_5.CH_2.MgCl + (C_6H_5)_3CCl = (C_6H_5)_3C.CH_2C_6H_5 + MgCl_2.$$

Triphenylchloromethane forms two isomeric magnesium compounds; the α-form possibly has the formula—

and the β-form—

$$(C_6H_5)_3C.MgCl,$$

each one of which appears to interact with triphenylchloromethane to give triphenylmethyl. The bearing of these isomeric compounds on the constitution of triphenylmethyl is at present under discussion (Schmidlin, *Ber.*, 1907, xl., 2316).

Acids.

(*a*) *Carboxylic Acids.*—Grignard was the first to study the action of carbon dioxide on magnesium alkyl halides (*Annales de l'Université de Lyon*, 1901, vi., 1; *Ann. Chim. Phys.*, 1901, [7], xxiv., 435). He found, for example, that when a current of carbon dioxide is passed through an ethereal solution of magnesium methyl iodide, and the product then decomposed by dilute acid, acetic acid is formed :—

$$CH_3MgI + CO_2 = CH_3.COOMgI,$$
$$CH_3.COOMgI + H_2O = CH_3.COOH + MgIOH.$$

This action has been extensively applied, amongst others, by Zelinsky (*Ber.*, 1902, xxxv., 2687, 2692, 4415; 1903, xxxvi., 208), Bodroux (*Bull. Soc. Chim.*, 1904. [3], xxxi., 30), and especially by Houben. It has already been pointed out, however, that, under certain conditions, a carboxylic acid may result from this action either in very small yield or not at all (see section on Tertiary Alcohols). The method, however, in most cases is very successful. Houben gives it as a general one for making aromatic and hydroaromatic carboxylic acids; terephthalic acid, for example, is readily obtained from *p*-dibromobenzene. The yields are often exceedingly good; for example, Schmidlin (*Ber.*, 1906, xxxix., 628) obtains an 83 per cent yield of triphenylacetic acid from triphenylchloromethane.

The action of the Grignard reagent on ethyl chlorocarbonate proceeds in two phases (Houben, *Ber.*, 1903, xxxvi., 3087), *e.g.*,—

$$(1)\ C_6H_5MgBr + Cl.COOC_2H_5 = C_6H_5.COOC_2H_5 + MgClBr,$$
$$(2)\ C_6H_5.COOC_2H_5 \rightarrow (C_6H_5)_3C.OH.$$

Under suitable conditions, *i.e.*, by avoiding an excess of the Grignard reagent, ethyl benzoate is formed; so that we have here another method of converting bromobenzene into benzoic acid, in addition to the one which involves the use of carbon dioxide.

The following method has been applied for obtaining hydroxy-acids. The action of the Grignard reagent on the ester of a ketonic acid may be so regulated that the carbonyl group is attacked, whereas the —COOR group either survives the attack or is very slightly acted on; thus menthyl benzoylformate, $C_6H_5.CO.COOC_{10}H_{19}$, was converted by McKenzie (*Trans. Chem. Soc.*, 1904, lxxxv., 1261) into benzilic acid, $(C_6H_5)_2C(OH).CO_2H$, by means of magnesium phenyl bromide. The asymmetric synthesis of atrolactinic acid, $\begin{matrix}CH_3\\C_6H_5\end{matrix}\!>\!C\!<\!\begin{matrix}OH\\COOH\end{matrix}$, may be accomplished either from benzoylformic acid, $C_6H_5.CO.COOH$, or from pyruvic acid, $CH_3.CO.COOH$, by aid of the same reaction (McKenzie, *Trans. Chem. Soc.*, 1904, lxxxv., 1259; 1906, lxxxix., 365; McKenzie and Wren, *Ibid.*, 1906, lxxxix., 688).

Another example of a compound presenting two points of attack is afforded by ethylcyanoacetate. Here the —COOR group may survive the attack of the Grignard reagent, and by taking advantage of this Blaise was able to obtain esters of β-ketonic acids (*Comptes Rendus*, 1901, cxxxii., 38, 478, 978) :—

$$COOC_2H_5.CH_2CN + C_2H_5MgI \rightarrow COOC_2H_5.CH_2.C\!\leq\!\begin{matrix}N.MgI\\C_2H_5\end{matrix} \rightarrow COOC_2H_5.CH_2.CO.C_2H_5.$$

(Compare Blaise's method for the preparation of ketones, see later).

(*b*) *Sulphur Acids.*—Sulphinic acids are formed by the action of sulphur dioxide (Rosenheim and Singer, *Ber.*, 1904, xxxvii., 2152), *e.g.*, benzenesulphinic acid is obtained from magnesium phenyl bromide :—

$$C_6H_5MgBr + SO_2 = C_6H_5.SO_2MgBr$$
$$C_6H_5.SO_2MgBr + H_2O = C_6H_5.SO_2H + MgBrOH.$$

Another method of obtaining sulphinic acids is described by Oddo, who uses sulphuryl chloride (*Atti R. Accad. Lincei*, 1905, [5], xiv., I., 169). Benzenesulphinic acid is produced according to the scheme :—

$$(1)\ SO_2Cl_2 + C_6H_5MgBr = C_6H_5.SO_2Cl + MgClBr$$
$$(2)\ C_6H_5.SO_2Cl + C_6H_5MgBr = C_6H_5.SO_2MgBr + C_6H_5Cl$$
$$(3)\ C_6H_5.SO_2MgBr \rightarrow C_6H_5.SO_2H.$$

Weigert (*Ber.*, 1903, xxxvi., 1007), shows that thiolic acids are obtained from carbonyl sulphide, which, *e.g.*, with magnesium ethyl bromide, gives thiolpropionic acid: $COS + C_2H_5MgBr = CS(C_2H_5).OMgBr \rightarrow C_2H_5COSH$.

Carbithionic acids are described by Houben and his pupils (*Ber.*, 1902, xxxv., 3696; 1906, xxxix., 3219; 1907, xl., 1303, 1725), who substitute carbon disulphide for carbon dioxide, thus: $CH_3MgI + CS_2 \rightarrow CH_3.CSSMgI \rightarrow CH_3.CSSH$. Those interesting acids are yellow, red, or violet oils, rather unstable, strong acids, which are readily oxidised to the disulphides, R.CS.S.S.CS.R.

Ketones.

Nitriles were converted into ketones by Blaise, who obtains, *e.g.*, an 80 per cent yield of phenylethyl ketone from magnesium ethyl iodide and benzonitrile (*Comptes Rendus*, 1901, cxxxii., 38; cxxxiii., 299, &c.; compare also Béhal, *Bull. Soc. Chim.*, 1904, [3], xxxi., 461) :—

$$C_2H_5MgI + C_6H_5CN = C_6H_5.C\!\leq\!\begin{matrix}C_2H_5\\N.MgI\end{matrix}$$
$$C_6H_5.C\!\leq\!\begin{matrix}C_2H_5\\N.MgI\end{matrix} + H_2O = \begin{matrix}C_6H_5\\C_2H_5\end{matrix}\!>\!C{:}NH + MgIOH$$
$$\begin{matrix}C_6H_5\\C_2H_5\end{matrix}\!>\!C{:}NH + H_2O = NH_3 + C_6H_5.CO.C_2H_5.$$

The method, however, is not always so successful as in this particular case. Very varying yields were also obtained by Béis, who investigated the action on acid amides, which were heated for several hours with an excess of the reagent (*Comptes Rendus*, 1903, cxxxvii., 575). The action is represented as follows:—

$$R.CONH_2 + 2MgR'X = R.C(OMgX)(NHMgX)R' + R'H$$
$$R.C(OMgX)(NHMgX)R' + 2H_2O = = R.C(OH)(NH_2)R' + MgX_2 + Mg(OH)_2$$
$$R.C(OH)(NH_2)R' = R.CO.R' + NH_3.$$

I have been able to find in the literature very few cases where ketones have been obtained from acid chlorides; the latter, of course, readily yield tertiary alcohols. It is difficult to arrest the action in the first phase, $R'COCl + RMgX = R'.CO.R + MgXCl$. Acree obtains phenyl α-naphthyl ketone from benzoyl chloride and magnesium α-naphthyl bromide, but the yield is not stated (*Ber.*, 1904, xxxvii., 625). Gomberg and Cone obtain benzophenone in small yield from benzoylchloride and magnesium phenyl bromide (*Ber.*, 1906 xxxix., 2957).

Benzophenone may be obtained together with benzoic and triphenylcarbinol by the action of carbon dioxide on magnesium phenyl bromide, thus:—

$$C_6H_5MgBr \rightarrow C_6H_5.COOMgBr \rightarrow \rightarrow (C_6H_5)_2C(OMgBr)_2 \rightarrow (C_6H_5)_2CO$$

(Schroeter, *Ber.*, 1903, xxxvi., 3005; 1907, xl., 1584). But here, again, it has not been found possible to arrest the reaction so as to give a satisfactory yield of ketone. The method has also been applied by Bodroux for obtaining dibromo- and dichloro-derivatives of benzophenone (*Comptes Rendus*, 1903, cxxxvii., 710), but it cannot be quoted as a general method.

Kohler (*Am. Chem. Journ.*, 1904, xxxi., 642; 1905, xxxiii., 21, 35, 153, &c.; *Ber.*, 1905, xxxviii., 1203; compare Bauer and Breit, *Ber.*, 1906, xxxix., 1916) finds on studying the action of unsaturated ketones that if a methyl group is attached to the carbonyl group of the ketone the reaction proceeds in the same manner as with a saturated ketone; if, however, a phenyl group is attached to the carbonyl group, a ketone is produced. Thus cinnamylidene acetophenone, $C_6H_5.CH{:}CH.CH{:}CH.CO.C_6H_5$, does not form, with magnesium phenyl bromide, the tertiary alcohol $C_6H_5.CH{:}CH.CH{:}CH.C(OH)(C_6H_5)_2$, but gives β-phenyl β-styryl propiophenone,—

$$C_6H_5.CH{:}CH.CH(C_6H_5).CH_2.CO.C_6H_5.$$

Bauer (*Ber.*, 1904, xxxvii., 735; 1905, xxxviii., 240) obtains dialkylphthalides from phthalic anhydride; thus with magnesium methyl-iodide:—

$$C_6H_4\langle^{CO}_{CO}\rangle O \rightarrow C_6H_4\langle^{C(CH_3)_2}_{CO_2H}\rangle OH \rightarrow \rightarrow C_6H_4\langle^{C(CH_3)_2}_{CO}\rangle O.$$

α-Methyl phthalide, $C_6H_4\langle^{CH(CH_3)}_{CO}\rangle O$, is obtained from phthaldehydic acid (Simonis, Marben, and Mermod, *Ber.*, 1905, xxxviii., 3981).

(To be continued).

Alloys of Cobalt and Tin.—F. Ducelliez.—From mixtures of cobalt and tin containing less than 57 per cent of tin, an alloy can be separated which approaches in composition to the compound Co_3Sn_2. This alloy is a powder which has not a very distinct crystalline character. It is attracted by a magnet. Its density is found to be 8·86, while the calculated density is 7·79. In chemical properties it resembles CoSn, but the latter appears to be more susceptible to the action of hydrochloric acid, while equally resistant towards nitric acid.—*Comptes Rendus*, cxlv., No. 8.

CORRESPONDENCE.

A WARNING.

To the Editor of the Chemical News.

SIR,—I shall be much obliged if, through the medium o your columns, you will allow me to put analytical chemists on their guard against a man who has recently been calling upon members of the profession with a view to monetary assistance, passing himself off under my name, and stating that he has had to resign the post of Public Analyst for Warrington as he is suffering from incurable consumption. It is a gross case of impersonation.—I am, &c.,

FREDERICK G. RUDDOCK,
Public Analyst for the Borough of Warrington.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlv., No. 7, August 12, 1907.

This number contains no chemical matter.

No. 8, August 19, 1907.

Symmetric Dimethyl Ethylene Oxide,—

$$H_3C{-}CH{-}CH{-}CH_3 \quad (O)$$

—Louis Henry.—When methyl magnesium bromide acts upon symmetric dimethyl ethylene oxide, if the latter behaves like ethylene oxide, the product would be methyl isopropyl carbinol, $\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CH{-}CH(OH){-}CH_3$ (boiling-point 112°), but if the oxide isomerises a methyl ethyl ketone will be formed, giving rise to the tertiary alcohol, dimethyl ethyl carbinol, $(CH_3)_2{=}C{-}CH_2{-}CH_3$ with OH (boiling-point 102—103°). The author has found that the latter alcohol is the product of the reaction, *i.e.*, butylene oxide, $CH_3{-}CH{-}CH{-}CH_3$ (O), gives with methyl magnesium bromide the same alcoholic compound as its isomer, $CH_3{-}CO{-}CH_2{-}CH_3$.

Liberation of Emanation by Radium Salts at different Temperatures.—L. Kolowrat.—If a salt, *e.g.*, radium chloride, is fused, all the emanation which is accumulated in it can readily be extracted. If all the emanation contained in a salt is thus removed, the tube is then closed, and a definite temperature maintained; the quantity of emanation liberated after a definite time is a function of the temperature. This quantity is small at the ordinary temperature, and equal to about 1 per cent of the total amount; on raising the temperature it remains constant at 350°; then increases rapidly, and reaches 90 per cent at 830°, afterwards decreasing to 60 per cent at 920°, and again rising to 100 per cent at 945°, the melting-point of the chloride. The decrease before fusion also occurs in the case of the fluoride.

Alloys of Nickel and Tin.—Em. Vigouroux.—Alloys of nickel and tin containing 57·65 to 66·76 per cent of the latter have been subjected to the action of hydrochloric acid, in order to separate Ni_3Sn_2, and to nitric acid to eliminate NiSn. It is found that these alloys generally lose tin in the former case, tending to the limit 57·65, which corresponds to the formula Ni_3Sn_2, but when treated with nitric acid they approach the limit 66·76, which is

that of the substance NiSn. Thus, the general results of the author's work on these alloys are as follows :—Alloys of nickel and tin are magnetic when the percentage of tin lies between 0 and 40·22 (this number corresponding to Ni_3Sn) ; their brittleness increases as the amount of tin is increased, the maximum occurring between 40·22 (Ni_3Sn) and 66·76 (NiSn). After this it diminishes. At 85 per cent the alloys are to a certain extent malleable.

Action of Certain Substances upon Potassium Iodide.—B. Szilard.—Many substances, *e.g*, the oxides of uranium, thorium, iron, cobalt, &c., which are insoluble in water, have the power of acting on a solution of potassium iodide, setting free a certain amount of iodine; this reaction takes place even in an atmosphere of carbon dioxide. The same effect is produced by certain minerals, *e.g.*, fergusonite, cleveite, pitchblende. The degree of decomposition is very variable, and does not seem to be simply connected with the composition of the mineral. Certain uranium minerals (fergusonite, pitchblende) have a great activity, while others (thorianite, orangeite) have none at all. Joachimsthal pitchblende has the greatest activity, and with it contact is not absolutely necessary, for if paper is soaked in potassium iodide solution and starch, and placed above damp pitchblende in a closed vessel, it becomes blue. Pitchblende does not decompose potassium bromide or chloride, and experiments have shown that there is no connection between its radioactivity and its action on potassium iodide.

New Sensitive Method of Detecting Nickel.—Emm. Pozzi-Escot. — Nickel molybdate, obtained by the double decomposition of an alkaline molybdate and a nickel salt, is insoluble in a neutral or feebly acid aqueous solution which contains a sufficient excess of alkaline molybdate, while cobalt molybdate is very soluble under the same conditions. This reaction can therefore be used to detect nickel in presence of cobalt. Other metals, such as zinc, cadmium, manganese, also give a precipitate, but they can readily be eliminated by other methods. It is quite easy to detect 1 centigrm. of nickel in presence of five hundred times its weight of cobalt. The only case in which this method is not applicable is when the cobalt is present as a salt of cobaltamine, when it is at once precipitated; it must, however, be remembered that cobaltamine salts are readily converted into cobalt salts. The same method can be used for the microchemical detection of nickel, although zinc molybdate resembles the nickel salt closely.

Preparation of Asymmetric Halogen Hydrines and Properties of Corresponding Oxides of Ethylene.—MM. Fourneau and Tiffeneau.—The α-halogen hydrines can be prepared by the action of organomagnesium compounds upon either chloracetone chloracetic ether or their homologues. Mostly secondary products with boiling-points very close to those of the chlorhydrines are also formed, but the latter can be isolated by treating the raw product of the reaction either with potash, which converts the chlorhydrine into ethylene oxide, or with dimethylamine, which converts them into amino alcohols, soluble in acids. When an organo-magnesium derivative acts upon asymmetric disubstituted ethylene oxides the reaction which occurs may be represented by the equation $\begin{matrix}R\\R\end{matrix}\!>\!C\!-\!CH_2 + BrMgR' \rightarrow RR=CH-CHOH-R'$.

With monosubstituted ethylene oxides the reaction is $R-\underset{\backslash O/}{CH}-CH_2 + BrMgR' \rightarrow R-CHOH-CH_2-R'$.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xl., No. 12, 1907.

Use of Palladium as a Contact Substance in Elementary Analysis.—Arnold Jacobsen and Georg Landesen.—Palladium is more suitable for use as a contact substance in elementary analysis than platinum. It is readily oxidisable at a high temperature, and equally easily reduced when the temperature is further raised, or in presence of oxidisable substances; it removes the hydrogen from hydrocarbons at a red heat, depositing carbon, which may be completely burnt on the admission of air. The authors have found that it is best to use it in the form of asbestos, made by precipitating a solution of pure palladous chloride in presence of asbestos by sodium formate in alkaline solution, and then completely washing out the soluble salts. A potash glass tube of diameter about 1 cm. is drawn out so that a constriction with diameter about 0·5 cm. is made a few cm. from one end. The narrow part of the tube is filled with palladium asbestos, which is kept in place by a perforated clay plug. The substance to be burnt is placed in a porcelain boat behind the palladium asbestos, and the tube is connected with a gasometer containing oxygen. Before beginning the combustion the narrow part of the tube, and also the end which is to contain the porcelain boat, is heated. Then pure dry oxygen is led in, and the tube is allowed to cool; the boat is then introduced, and a current of oxygen allowed to pass, the palladium asbestos being meanwhile heated. The degree to which the part of the tube containing the boat is heated is regulated by the nature of the substance, and its volatility also decides the relative nearness of the boat to the asbestos, more volatile substances being placed further from the palladium, and care being taken that no condensation occurs between the boat and the palladium. The boat is preferably long and narrow in shape, and when the substance fuses before volatilising it must be evenly distributed throughout the boat. In the case of substances which are not very volatile, or volatilise with gradual decomposition, it is not necessary to use a tube with a constriction; equally good results being obtained with a tube which has not been drawn out.

Cobaltic Nitrites.—K. A. Hofmann and O. Burger.—When the aqueous solution of the cobalt ethyl ammonium salt, $[Co(NO_2)_6][AmH_3]$, is precipitated with excess of silver nitrate, and the dry silver salt is treated with ethyl iodide in dry ether, after warming for some time silver iodide separates, and ethyl nitrite results, while no nitroethane is formed. Hence, it may be deduced that the structure of the nitrous acid in the cobaltic nitrite is normal, but no definite proof of this is thus afforded. To prepare the nitrito-cobaltic acid ammonium, $[Co(NO_2)_6](NH_4)_3$, cobalt carbonate is suspended in 8 per cent aqueous ammonia, and the vapours from solid sodium nitrite and fuming nitric acid led in, meanwhile cooling with ice, until all the cobalt salt has disappeared; the liquid is dark brown, and the yellow salt is precipitated in considerable quantity. When this yellow salt, nitritocobaltic acid ammonium, is decomposed, it is found from the amount of nitrogen set free that it contains three normal nitrous acid residues bound to the ammonium. This result is completely confirmed by the investigation of the ethyl ammonium salt, $Co(NO_2)_6.(NH_3C_2H_5)_3$, which has now been prepared for the first time by leading nitrous acid gas into a cooled mixture of cobalt carbonate, water, and ethylamine solution.

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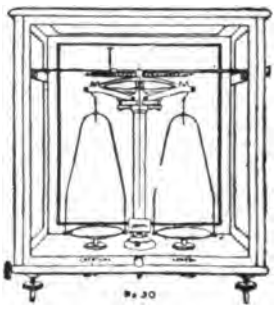

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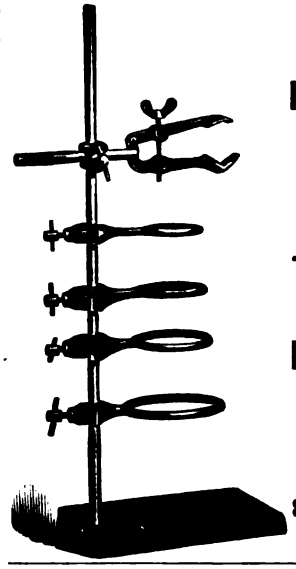

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THE CHEMICAL NEWS.

Vol. XCVI., No. 2497.

THE DEPOSITION OF METALLIC SILVER UPON GLASS.

Short Studies in Chemical History (II.).

By F. D. CHATTAWAY.

(Concluded from p. 153).

The glass speculum to be silvered, having been attached by pitch to a wooden block containing three eyes screwed into it by which it can be suspended face downward in the liquid, is next most carefully cleaned successively with strong nitric acid and caustic potash, and washed thoroughly with distilled water. It is then immersed in the silvering fluid face downwards, using so much fluid that a layer about half an inch in depth is interposed between its surface and the bottom of the vessel. When the silvering is complete, which will take from sixty to ninety minutes, according to the temperature, the speculum is removed from the solution, immediately washed with plenty of distilled water, and placed on its edge upon blotting-paper to drain and dry.

When perfectly dry, the film is polished by gently rubbing with a piece of soft wash-leather, using circular strokes, and the operation is completed by the use of a little of the finest rouge.

When tarnished the brilliancy of the silver can be easily restored by re-polishing, and should the film of metal become detached or spoiled, it may easily be removed and a fresh one deposited without in any way impairing the figure or polish of the glass speculum. A plane surface can, of course, be silvered similarly.

Although Liebig's method of silvering glass was for a long time almost exclusively used in practice, a number of investigators busied themselves with the elaboration of new processes. These, however, differ from Liebig's, and also from each other, only in the agent used to reduce the dissolved silver oxide. Many substances have been recommended for the latter purpose, but only milk and grape-sugar, invert sugar, tartrates, aldehyde, ammonia, and formaldehyde have come into actual use.

The reducing liquid which has received the most extensive practical application in recent years is a solution of Rochelle salt, which has been mixed with a quantity of silver nitrate and boiled.

This solution was introduced by Dr. Ferd Bothe in preference to Rochelle salt itself (*Journ. Prakt. Chem.*, 1864, xcii., 191), though according to Claus (*Ber.*, 1875, viii., 948) it contains very little besides silver tartrate.

Bothe originally recommended that the reducing liquid should be prepared by precipitating silver tartrate, and boiling this with water, when blackening takes place, and the larger part goes into solution, forming a strongly reducing liquid. Bottger (*Polytech. Notizbl.*, 1864, 300) a few months later suggested that this liquid could be made more conveniently by adding a solution of silver nitrate to a hot solution of Rochelle salt, boiling the whole for about ten minutes, cooling, and filtering.

Kayser, in 1890 (*Zeit. Angew. Chem.*, 1890, 541), stated that, in spite of the greatly increased use of silver mirrors in recent years, no process had in practice proved invariably successful in producing large ones without flaws; he therefore gave the following detailed directions for the preparation and use of a mixed reducing solution which he had found to give uniformly good results.

To prepare the silver solution 10 grms. of silver nitrate are dissolved in 50 cc. of distilled water, and a pure solution of ammonia is dropped in till the precipitate first formed is just dissolved. Then, in order to avoid any excess of ammonia, a somewhat weak solution of silver nitrate is added until a slight opalescence appears, and the whole diluted to 1 litre. The solution is finally filtered, or, as is preferable, allowed to stand some time till it is quite clear.

To prepare the reducing fluid, 20 grms. of Rochelle salt and 20 grms. of pure white cane-sugar are dissolved in 200 cc. of distilled water, and a solution of 4 grms. of silver nitrate in 20 cc. of water added. The mixed liquids are shaken vigorously and boiled gently for half-an-hour; the hot mixture is then immediately diluted to 1 litre with cold distilled water, and, after well shaking, filtered.

For filtering purposes, equal volumes of the two liquids are mixed, and immediately poured on the plate to be coated, to a depth of from 1·5 to 2 cm. The deposition of silver begins almost at once, and is complete in from fifteen to twenty minutes. If the metallic film is not sufficiently thick the operation can be repeated. The plate, after thoroughly washing, is allowed to stand upright till completely dry. It may then be carefully varnished with a dilute alcoholic solution of shellac, and after this has thoroughly hardened, a second coat of a similar varnish, to which some indifferent colouring matter has been added, may be applied.

A very simple process, in which formaldehyde is used as the reducing agent, was described in 1894 by Auguste and Louis Lumière (*Séances de la Société Francaise de Physique*, 1894, 264). The silvering liquid used is prepared by dissolving 10 grms. of silver nitrate in a little water, adding ammonia drop by drop until the precipitate at first formed is re-dissolved, and diluting to 1 litre. As much of this as is necessary is mixed with half its volume of a 1 per cent solution of formaldehyde, prepared by diluting the commercial 40 per cent solution, and poured upon the surface to be silvered to a depth of 1 to 2 cm. After five to ten minutes at the ordinary temperature all the silver is deposited as a coherent layer which, after washing and drying, can be either polished or varnished.

Most of the processes which have been recommended will, if carefully carried out, give good results, and it appears largely a matter of preference which should be adopted for any purpose.

Ostwald and Luther in their "Hand- und Hülfsbuch zur Ausführung Physiko-Chemischer Messungen (Leipzig, 1902) recommend a modification of a method proposed by Adolphe Martin in 1868 (*Ann. de Chim. et de Phys*, 1868, [4], xv., 94), and give the following instructions:—"Dissolve 90 grms. of pure sugar in a litre of water, and add to it 175 cc. of alcohol and 4 cc. of nitric acid of density 1·2. Allow the solution to stand for at least a week before use. Shortly before it is required dissolve 1 grm. of silver nitrate in 100 cc. of distilled water, add 1 cc. of a strong solution of ammonia of density 0·9, and then, drop by drop shaking continuously, a more dilute solution of ammonia (about 1 volume concentrated solution of ammonia and 5 volumes of water) until the precipitate is just dissolved. Add then half a gram of caustic potash (purified by alcohol and as far as possible free from carbonate) dissolved in 50 cc. of water, and again drop in cautiously the diluted solution of ammonia until nearly all the re-precipitated oxide disappears. Allow the slightly cloudy brownish coloured liquid to stand for some time, and filter through cotton-wool.

"In order to carry out the silvering mix 150 cc. of the silver solution with 6 cc. of the sugar solution, and pour it over the surface to be covered. One grm. of silver nitrate is sufficient to silver 40 square centimetres. At a temperature of about 20° C. the reduction is completed in ten to fifteen minutes. When the deposition of silver is finished the plate should be throughly washed with water and carefully dried. It may afterwards be polished if it is desired that it should reflect from the metallic surface."

The successful silvering of glass depends above everything upon the perfect polish and cleanliness of the surface. Blown glass which has not been touched can be silvered much more easily than polished. If the glass has been

kept for any length of time it will not take the silver properly without re-polishing. The surface immediately before silvering should be throughly washed, using in succession hot soap solution, strong nitric acid, and a strong solution of caustic potash. The surface should be thoroughly rubbed with each liquid by means of a pad of cotton-wool tied to a glass rod, or better partially thrust tightly into one end of a glass tube. Between each successive cleansing the plate should be thoroughly washed with clean water, and just before being placed in the silvering fluid it should be well rubbed over with it and wetted in every part, using a pad of cotton-wool soaked with the liquid.

The purity of the materials employed is also of the highest importance. Chlorides, either in the chemicals or in the water used, are especially to be avoided. The alkali, both the ammonia and the potash, must be as far as possible free from carbonate, as the latter is found to cause considerable reduction to take place in the bath itself, and thus to diminish the quantity of silver deposited upon the glass; it also appears to produce upon the silvered surface white flecks which cannot be removed.

The surface after silvering must be very carefully washed, as if the last traces of the silvering fluid are not removed they are liable to cause stains and defects to develop later in the mirror.

The film of silver must on no account be touched until it is perfectly dry, and even after drying and polishing it is always very sensitive to damp. The specula of reflecting telescopes, for example, if they have been exposed to damp air or dew, should always be dried in the most thorough manner before they are re-polished or touched in any way.

When a large surface has to be silvered, as in the manufacture of mirrors, the plate having been carefully levelled, the silvering fluid is poured directly upon it, the surface tension being sufficient to prevent a layer of the depth required running off at the edges. The room where the glass is silvered must be kept free from all dust, and its temperature should not be allowed to fall below 20° C.

Although silvered glass mirrors, when properly made, are far more durable than mercurial mirrors, and reflect much better with a loss of only about 10 per cent of the light falling upon them, they yet possess one property, which is sometimes regarded as a defect. Like mirrors of polished silver, they show the slightest trace of a yellow colour. It is, of course, impossible to avoid this when silver is used. If one looks at the sun through a thin deposit of silver upon glass, its disc appears of a blue colour, while if the layer is very thin it is as though one looked through blue glass. Silver therefore allows blue rays to pass through and become absorbed, while light of other refrangibilities is reflected. White light when reflected from a silver surface must therefore lose a certain proportion of its blue rays, and since the yellow rays are no longer completely compensated the reflected light has a slightly yellow colour. A yellowish tint is thus given to any white object seen mirrored in silver.

This supposed defect has prevented to a large extent the replacement of mercurial by silvered mirrors in France, and attempts have been made to overcome it by treating the film of silver deposited in the ordinary way with various mercury salts, and thus converting it into amalgam.

Drautz has suggested another method, and in 1891 patented a process (D.R.P. 56,260) for obtaining a silver deposit with a bluish tint by using a reducing solution containing a little of a lead salt.

In spite of the large amount of work which has been done on the reduction of silver salts in connection both with mirror making and with photography, very little is known as to the reason why, when silver oxide is reduced under certain conditions, the metal is deposited on the glass in the form of a brilliantly reflecting coherent film, while under others apparently equally favourable to such deposition it separates in a spongy or flocculent state.

Vogel (*Journ. Prakt. Chem.*, 1862, lxxxvi., 321) concludes from his experiments that when complete reduction of the oxide takes place in one stage, a mirror or a crystalline deposit of silver is obtained, while granular or finely divided silver is produced in two stages, a lower insoluble oxide of silver separating as the primary product of the reduction and being afterwards itself reduced.

The assumption of reduction in two stages appears, however, unnecessary, and in no way explains the circumstance that mirrors are never formed, or only with great difficulty, in an acid solution. For the silver to separate entirely on the surface of the glass it is necessary for it to be deposited from a clear solution containing no metallic particles to act as nuclei for deposition in the body of the liquid, nor any solid particles of oxide able on reduction to form such.

It seems probable that an explanation must be sought in some catalytic action of the glass surface which locally accelerates reduction in alkaline solution.

Oberbeck some years ago (*Ann. der Physik. und Chem.*, 1892, xlvi., 265) measured the electric resistance of a thin mirror of silver deposited from aqueous solution upon glass. His results show that the electric resistance of such films is very large immediately after deposition, but that it continually diminishes with time, and has not reached a minimum even after two years. He notes that this diminution in the resistance takes place whether the films are thick with a good reflecting surface or thin and semi-transparent. The actual resistances of the different films measured by Oberbeck varied originally from 19·7 ohms to 633·7 ohms, the resistances of this pair of films diminishing in 641 days to 2·84 and 58·4 ohms respectively.

In spite of such great alterations in resistance the mirrors showed no change either in reflecting power or in appearance when viewed by transmitted light.

Oberbeck concluded that his observations could only be explained by assuming that the silver so deposited is, when first laid down, in a different molecular condition from ordinary silver, but that its condition approaches that of the latter more and more with time.

SIMPLE MODELS OF TETRAHEDRAL CARBON ATOMS.

By R. V. STANFORD, M.Sc.

Both for lecture demonstration and for the study of stereochemical questions the possession of a set of models of tetrahedral carbon atoms is of great convenience to the chemist. Such models are readily constructed in any number in the following way:—

A piece of close-grained wood, such as canary wood, is planed into a strip of triangular section, each side being 2 cm. wide. One end is "squared," and a line is cut round the strip 1·63 cm. from this face. The middle point of the triangular end-face is then found and marked with a pencil point, and each side is cut down to it from the line. In this way three of the sides of a regular tetrahedron are produced. The tetrahedron is now sawn off the strip and the remaining face produced by cutting down to the mark previously made round the strip.

Some thin steel-wire is then taken—that used for making wire-brushes is convenient—and cut into 3 cm. lengths, which are driven into the tetrahedron at the corners with the aid of a pair of pliers. Care should be taken that the wires are so inserted as to be perpendicular to the opposite faces of the tetrahedron.

In constructing the space model of a compound with these atoms the bonds are united by means of small pieces of cork, and the atoms are so light that quite complicated models may easily be built up with them. Owing to the elasticity of the steel-wires, they are also well adapted for showing the applicability of Baeyer's tension theory to the polymethylene derivatives; a trimethylene ring, for instance, splits instantly apart when one of the uniting corks is somewhat loosened.

Chemical Department, University of Birmingham.

ON THE DENSITY CURVE OF MIXTURES OF BROMINE AND CHLORINE.*

By LAUNCELOT W. ANDREWS and HENRY A. CARLTON.

The fullest determinations of the densities of bromine at various temperatures appear to be those of Thorpe (*Journ. Chem. Soc.*, 1880, xxxvii., 172) and of Pierre (Moissan, "Traité de Chimie Minérale," i., 133; *Ann. Chim. Phys.*, 1847, [3], xx., 45). The former determined the density at 0° to be 3·187, while Pierre found at the same temperature 3·188. At 35° Thorpe found 3·10104 and Pierre 3·10472 (Interpolated). We shall bring forward evidence in the present paper going to show that the results of Thorpe are too low by an amount which can be accounted for on the assumption that his bromine contained about 0·039 per cent of chlorine. The density of liquid chlorine at 25°, as calculated from the formula of Knietsch, is 1·39778 (*Annalen*, 1890, cclix., 100). The existence of a monochloride of bromine is generally assumed, on the basis of the investigations of Bornemann (*Annalen*, 1877, clxxxix., 206). There seems to be but little evidence to support this assumption, except the existence at low temperatures of hydrates, said to have the formulæ $BrCl.5H_2O$ and $BrCl.10H_2O$ (Loewig, "Das Brom," 64, Heidelberg, 1829). Obviously the existence of such hydrates, even if fully demonstrated, would constitute no sufficient proof of the existence of the compound BrCl in the absence of water. Proof or disproof of the existence of compounds of chlorine and of bromine with one another must be sought for in the physical properties and behaviour of mixtures of these elements at ordinary or at low temperatures. Among the properties to be taken into consideration in this connection is that of density. If it should appear that these elements mix without contraction of volume, that fact alone would be strong presumptive evidence against the existence of a compound. The chief object with which the authors undertook an investigation of the density curve of chlorine-bromine mixtures was a purely practical one. A simple preliminary calculation showed that, unless a very considerable contraction occurs on mixing chlorine with bromine, small percentages of chlorine must so greatly reduce the density of bromine as to make it possible to base on the density alone a determination of the chlorine with the prospect of very satisfactory results. This anticipation was fully realised.

In the density determinations three pycnometers were used by the authors, of which two were of the well-known Squibb type, with narrow divided stem, ground into the body, of 50 and 25 cc. respectively.

The values of the stem divisions were found by calibration with mercury, the capacity of the bulbs by weighing with water. The third instrument, made by Koehler, of 35 cc. capacity (nominal), is a constant volume instrument with the thermometer fused in the bulb. The readings of this, as of all other thermometers used, were carefully controlled.

It was not found possible by re-grinding the joints of the Squibb pycnometers to absolutely prevent evaporation of bromine. The loss was, however, small and was checked by weighing both before and after acquiring the temperature at which the scale reading was taken. It was observed that in two of these instruments the weight of the bromine caused the bottom of the bulb to bulge a little, increasing the volume above what it was when calibrated with water. The amount of this error was determined by immersing the pycnometer, filled with bromine, in a liquid of about the same density (acetylene tetrabromide) and comparing the reading with that obtained when the instrument was immersed in water, both liquids being in the same thermostat at identical temperatures. The maximum error due to this cause amounted to about five units in the fifth decimal place. No attempt was made to correct for it. If greater accuracy should be aimed at in future work, only pycnometers of spherical form, made rather thick in the wall and not flattened at the bottom, should be used. Very accurate thermometer readings would then become necessary. Some of the determinations referred to below were made at various temperatures between 25° and 32°. Those which were relied on for determinations of the constants of the formula were made in a thermostat within a few tenths of a degree of 25°, so that the correction for reduction to this temperature was small.

The weights used were corrected by comparison with a set of which a table of corrections had recently been furnished by the Bureau of Standards. Two thermometers were used. Their readings were reduced to the international hydrogen standard, on the basis of comparison with an instrument standardised by the Reichsanstalt and further controlled by observations at the zero point and at the transition point of sodium sulphate (after Richards). Both harmonised well. They were divided into one-fifth degree, but were read with a glass to one-fiftieth, with a probable error of about this amount. In consequence of the high coefficient of expansion of bromine, uncertainties in the temperature determinations become the chief source of error and practically set the limit to the accuracy of the results obtained.

The apparent coefficient of expansion of bromine in glass over the range 25° to 30° was found by us to be 0·00110, in excellent agreement with the results of Thorpe (*loc. cit.*). This factor was used in reducing observations made at other temperatures to the 25° standard, and we have assumed it to be valid for the impure as well as for the pure bromine. That this assumption is not too far from the truth within the limits of concentration to which it was applied is confirmed by a single determination of the coefficient for a bromine containing about five per cent of chlorine, which gave the value, 0·001128.

The density of pure bromine was determined on four preparations made from material derived from different sources and purified by different methods. The results are: Series A, 3·1022, 3·1019, 3·1022, 3·1019; Series B, 3·10143: Series C, 3·10218, 3·10230; Series D, 3·1025, 3·1027, 3·1025. Preparation B was partially frozen (melting point, −7·1°), the liquid portion poured off and the crystals used for the determination. An accident prevented its further examination, but although the density found is certainly too low, the figures are given, since the cause of the error is unknown. Series D is regarded as the most reliable, because the temperature determinations are more precise, the temperature corrections much smaller, and, further, because the material was shaken with calcium carbonate to remove possible traces of hydrobromic acid. In series A the bromine was dried with sulphuric acid, in the other series with phosphoric anhydride. Preparations A and D were known to be chlorine-free. They were tested by the method recently given by one of us (*Journ. Am. Chem. Soc.*, xxix., 275). Equal confidence is felt that Preparations A and B were also free from chlorine because of the guarantee afforded in the light of our experience with the method of preparation employed. The melting-point of Preparations A, C, and D was 7·0°, and the boiling-point 58·7° at 763 mm.

Probably the most persistent contamination of bromine is hydrobromic acid. We have not been able to devise any method for its removal which is not open to criticism. It should be said that Preparation D, after drying, &c., was re-distilled in two large fractions and a third, smaller, one. The first two had identical densities, the third a slightly lower one. Perhaps it is permissible to assume that all or a great part of the hydrobromic acid originally present was concentrated in the last fraction.

If double weight is assigned to Series D, and the one doubtful observation of Series B is not omitted from consideration, we obtain as the most probable value of the density of pure dry bromine from our observations $D\ 25°/4° = 3·10227$. With the aid of this constant for bromine and of the corresponding figure for chlorine of

* Read at the New York Meeting of the American Chemical Society. From the *Journal of the American Chemical Society*, xxix., No. 5.

Knietsch previously referred to, the theoretical relation of chlorine percentage (p), in a mixture of the two elements, to the density at 25° (d) of the mixture is given by the formula—

$$p = 82{\cdot}005\left(\frac{3{\cdot}10227}{d} - 1\right) \quad . \quad . \quad . \quad . \quad 1$$

on the assumption that no contraction occurs. We find that an expression of the same form, with a change in the coefficient of the second term, reproduces the observation values very well; to wit—

$$p = 88{\cdot}593\left(\frac{3{\cdot}10227}{d} - 1\right) = \frac{274{\cdot}840}{d} - 88{\cdot}593. \quad . \quad 2$$

When the mixture is saturated with water, the formula becomes—

$$p = 88{\cdot}59\left(\frac{3{\cdot}1004}{d} - 1\right) = \frac{274{\cdot}665}{d} - 88{\cdot}59 \quad . \quad . \quad 3$$

The last expression (3) must be regarded as merely approximate in character, since, as is well known, bromine and water react, producing hydrobromic acid and hypobromous acid. Hence, with the duration of contact the apparent solubility of water in the bromine steadily increases. When the relative amount of water is small the phenomenon is most marked, and the density of the bromine continues to decrease for a long time as it takes up hydrobromic acid and water. Equation 3 is approximately correct for bromine which has been quickly saturated at 25° with water by violent shaking.

The degree of precision of Equation 2 when applied to mixtures of pure bromine with pure chlorine is shown by the following comparison of the chlorine percentages of such mixtures as deduced by analysis (*Journ. Am. Chem. Soc.*, xxix., 275), and as calculated by the formulæ from the observed densities.

Per cent by analysis.	Density dry.	Per cent by Equation 2.	Density wet.	Per cent by Equation 3.
4·388				
4·461				
4·439	2·9553	4·406	2·9535	4·406
4·442				
4·407				
4·401				
7·741	2·8533	7·730	2·8512	7·743
7·717				
7·198			2·8661	7·242

The organic and other impurities, aside from chlorine, which are usually present in crude bromine, do not very seriously influence the results of the density determinations, as may be seen from the following analyses of material of this sort.

Per cent of Cl—	1.	2.	3.	4.	5.	6.
By density .	4·137	0·070	5·485	0·000	4·294	6·06
By analysis.	4·165	0·051	5·580	0·012	4·400	6·22

It is possible, therefore, to determine from the density of a sample of bromine the amount of chlorine it contains with sufficient accuracy for almost any purpose and in much less time than by any chemical method.

The contraction that occurs on mixing (liquid) chlorine with bromine can be readily calculated from Equation 2. The validity of this formula has only been tested to 11 per cent of chlorine, but if we extrapolate to 30 per cent (corresponding in composition approximately to BrCl) it gives for the corresponding density 2·4175, whereas, if no contraction occurred the density would be 2·2713. The contraction amounts, accordingly, to about 2 per cent of the total volume, a result that appreciably increases the probability that actual chemical combination does take place between these elements to a limited extent.

In conclusion, we present the following comparison of the densities of bromine at several temperatures as found by Thorpe and by Pierre with our own results.

Temp. °C.	Pierre (1847).	Thorpe (1880).	A. and C. (1906).
0	3·188	3·187	—
20	3·121(45)	3·118(43)	3·11932
25	3·104(72)	3·101(04)	3·10227
30	—	—	3·08479

ON THE

ARSENATE PROCESS FOR THE SEPARATION OF MAGNESIUM AND THE ALKALIS.

By PHILIP E. BROWNING and W. A. DRUSHEL.

Among the methods which have been employed for the separation of magnesium from the alkalis the following are perhaps in most general use:—

The barium hydroxide method, whereby the magnesium is precipitated as the hydroxide by barium hydroxide.

The mercuric oxide method, whereby the magnesia is precipitated by freshly prepared mercuric oxide acting upon the chlorides.

The ammonium carbonate method, whereby the magnesium is precipitated as the double carbonate of magnesium and ammonium by a large excess of ammonium carbonate (Wulfing, *Ber.*, xxxii., 2214).

The amyl alcohol method, whereby the magnesium chloride is dissolved in boiling amyl alcohol and the chlorides of sodium and potassium, not lithium, remain undissolved (Riggs, *Am. Journ. Sci.* [3], xliv., 103).

None of these methods, when employed with a view to the subsequent estimation of the alkalis, is free from objectionable features, such as difficulties of filtration, numerous transfers of filtrates, introduction of large amounts of reagents difficult of removal, and incomplete separation of the entire alkali group.

The work to be described is an effort to avoid some of the objections mentioned, by the precipitation of magnesium as the magnesium ammonium arsenate and the removal of the arsenate from the filtrate by reduction and volatilisation of the arsenic salt. C. v. Hauer (*Jahrb. der k. k. Geolog. Reichanstalt*, iv., 863) suggested this general procedure and it has found other mention in the literature (Fresenius-Cohn, "Quant. Anal.," 6th ed., vol. i., 613). The removal of the excess of arsenic was accomplished by ignition of the residue, obtained after evaporating the filtrate from the ammonium magnesium arsenate, with ammonium chloride. The method, however, has been criticised as inaccurate for the estimation of magnesium, and tedious. Recent work upon the precipitation of magnesium ammonium arsenate and upon the volatilisation of arsenic compounds suggested the possibility of obviating the difficulties which have kept this method from general use.

It is possible, with careful manipulation, to remove the arsenic by precipitating with hydrogen sulphide, but this procedure required an additional filtration and several transfers of liquid, and was therefore abandoned in favour of the separation by volatilisation.

The reagents used in this work were prepared as follows: The potassium chloride by igniting pure potassium chlorate and crystallising; the sodium chloride by re-crystallising the so-called pure sodium chloride. Solutions of these salts were made approximately tenth normal and standardised by evaporating measured portions with sulphuric acid in a weighed platinum crucible, and weighing the residues after ignition at the full heat of a Bunsen burner, as the normal sulphates.

A solution of magnesium chloride was obtained by dissolving a weighed amount of pure magnesium in hydrochloric acid and diluting sufficiently to make the solution approximately tenth normal. The solution was standardised by estimating the magnesium in measured portions as the pyroarsenate.

To obtain ammonium arsenate, arsenious oxide was sublimed and oxidised by an access of nitric acid. After

TABLE II.

	$(NH_4)_3AsO_4$ used, calculated as As_2O_5.	Dilution.	NaCl or KCl converted to Na_2SO_4 or K_2SO_4 and calculated as Na_2O or K_2O.			$MgCl_2$ converted into $Mg_2As_2O_7$ and calculated as MgO.		
			Taken.	Found.	Error.	Taken.	Found.	Error.
	Grm.	Cc.	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.
1.	0·1	100	0·1194	0·1191	−0·0003	0·0199	0·0197	−0·0002
2.	0·2	150	0·1194	0·1196	+0·0002	0.0399	0·0397	−0·0002
3.	0·45	250	0·1194	0·1195	+0·0001	0·0998	0·0998	—
4.	0·45	250	0·1194	0·1194	—	0·0998	0·0997	−0·0001
5.	0·45	250	0·2389	0·2385	−0·0004	0·0998	0·0999	+0·0001
6.	0·4	250	0·0478	0·0481	+0·0003	0·1198	0·1193	−0·0005
7.	0·35	250	0·0956	0·0957	+0·0001	0·0998	0·0996	−0·0002
8.	0·35	250	0·0956	0·0957	+0·0001	0·0998	0·0994	−0·0004
9.	0·45	250	0·0909	0·0915	+0·0006	0·0998	0·0993	−0·0005
10.	0·1	100	0·0545	0·0549	+0·0004	0·0006	0·0004	−0·0002
11.	0·1	100	0·1181	0·1184	+0·0003	0·0040	0·0038	−0·0002
12.	0·1	100	0·1181	0·1184	+0·0003	0·0040	0·0038	−0·0002
13.	0·1	100	—	—	—	0·0040	0·0038	−0·0002
14.	0·1	100	0·1181	0·1184	+0·0003	0·0040	0·0040	—
15.	0·2	100	0·1181	0·1183	+0·0002	0·0040	0·0039	−0·0001
16.	0·45	250	0·1181	0·1179	−0·0002	0·1002	0·1004	+0·0002

the completion of the oxidation, the excess of nitric acid was removed by evaporation, the residue treated with a slight excess of ammonium hydroxide, and the solution thus obtained diluted sufficiently to make it approximately fifth normal.

From a mixture of known amounts of standardised solutions of the chlorides of magnesium and potassium or sodium, the magnesium was precipitated in a distinctly but not strongly ammoniacal solution by 40 per cent to 80 per cent excess of ammonium arsenate, with brisk stirring. When only a small amount of magnesium is present in a relatively large amount of solution, the precipitate forms slowly and becomes complete only on long standing. In a previous paper from the Kent Chemical Laboratory of Yale University (Gooch and M. A. Phelps, *Am. Journ. Sci.*, 1906, xxi., 488), it has been shown that the precipitation of amounts of arsenic so small as not to be precipitated immediately by magnesium mixture may be brought about by freezing the solution after adding that reagent, and remains complete when melting takes place. This procedure was found equally applicable in the precipitation of magnesium. A similar result was obtained by adding alcohol amounting to 15 per cent to 20 per cent of the mixture and filtering as soon as the precipitate settled completely. The precipitate was collected under moderate pressure in an ignited and weighed perforated crucible containing a close felt of fine asbestos. It was washed with 40 to 50 cc. of ammoniacal water, after which it was dried at 125° C. to 140° C. and carefully ignited and weighed as magnesium pyroarsenate.

In a previous paper from the same laboratory, it has been shown that arsenic may be removed by distillation with potassium bromide and hydrochloric acid in a distilling apparatus (Gooch and I. K. Phelps, *Am. Journ. Sci.*, 894, xlviii., 216). This suggested a method for the removal of the arsenic from the filtrate obtained after separating the magnesium ammonium arsenate. In some preliminary qualitative experiments, solutions containing from 0·1 to 0·2 grm. of ammonium arsenate were treated with 10 cc. of hydrochloric acid (sp. gr. 1·20) and 10 cc. of hydrobromic acid (sp. gr. 1·36), or 1 to 3 grms. of ammonium bromide, and evaporated in an open dish and the residues were ignited until fuming ceased. One such treatment was usually found to be sufficient; in fact, simple evaporation on a steam bath with the mixed acids, or with hydrobromic acid (not with hydrochloric acid alone), proved to be sufficient to remove the arsenic. Similar treatments made in the presence of definite amounts of the sodium or potassium chloride gave the results shown in Table I.

TABLE I.

	Ammonium arsenate calculated as As_2O_5.	NaCl or KCl converted to Na_2SO_4 or K_2SO_4 and calculated as Na_2O and K_2O.		
		Taken.	Found.	Error.
	Grm.	Grm.	Grm.	Grm.
1.	0·2	0·1171	0·1172	+0·0001
2.	0·2	0·1171	0·1170	−0·0001
3.	0·4	0·1873	0·1870	−0·0003
4.	0·2	0·0468	0·0473	+0·0005

Some evaporations made with hydrochloric acid and sulphurous acid resulted in the removal of the arsenic, but three to five repetitions of the process were generally necessary.

The complete method as recommended for the estimation of magnesium and its removal from the alkalis, and the subsequent estimation of the alkalis, is as follows:—

The magnesium is precipitated in a distinctly but not strongly ammoniacal solution by a 40 per cent to 80 per cent excess of ammonium arsenate. The completeness of the precipitation may be hastened by freezing the solution in an ice and salt mixture or by adding alcohol to about 15 per cent to 20 per cent of the total volume of the solution, which may vary from 100 cc. to 250 cc. according to the amounts of salt present. The magnesium arsenate obtained is filtered on an asbestos felt contained in a perforated platinum crucible, the crucible and felt having been previously ignited and weighed, and is dried, ignited, and weighed as the pyroarsenate.

The filtrate is transferred from the filter flask to a platinum dish, and after the addition of 10 cc. of hydrochloric acid (sp. gr. 1·20) and about the same amount of hydrobromic acid (sp. gr. 1·3), or 1 to 3 grms. of ammonium bromide evaporated to dryness under a draught-hood, the residue is gently ignited to remove the ammonium salts. The residue is then transferred to a weighed platinum crucible with a small amount of water, a little sulphuric acid (1 : 1) added, and the solution evaporated to remove the water and excess of sulphuric acid, by placing the crucible on a triangle in a porcelain crucible used as a radiator. After the sulphuric acid has ceased to fume, the crucible is removed from the radiator, and after ignition at the full heat of the Bunsen burner the alkali is weighed as the normal sulphate. The results are given in Table II.

In experiments 1 to 10, the precipitate of magnesium was allowed twelve to twenty-four hours to settle. In experiments 11, 12, and 13, 15 per cent alcohol was used to hasten the complete precipitation of the magnesium,

and in experiments 14, 15, and 16 the salt and ice mixture was used for the same purpose.—*American Journal of Science*, xxiii., p. 293.

THE

APPLICATIONS OF GRIGNARD'S REACTION.*

By ALEX. McKENZIE, M.A., D.Sc., Ph.D.

(Continued from p. 161).

Section I. (*continued*).

Aldehydes.

Aldehydes are obtained, according to Bouveault (*Comptes Rendus*, 1903, cxxxvii., 987), from disubstituted formamides :—

$$H.CONRR' + R''MgX = HCR''(OMgX).NRR'$$

$$HCR''(OMgX).NRR' + H_2O = = R''.CHO + NHRR' + MgXOH.$$

Benzaldehyde, for example, was formed from ethyl formanilide and magnesium phenyl bromide.

Bodroux prepared a number of aldehydes in satisfactory yields from ethyl orthoformate (*Comptes Rendus*, 1904, cxxxviii., 92, 700; compare Tschitschibabin, *Ber.*, 1904, xxxvii., 186, 850). Benzaldehyde, for example, was obtained in a 90 per cent yield :—

$$CH(OC_2H_5)_3 + C_6H_5MgBr = MgBr(OC_2H_5) + C_6H_5.CH(OC_2H_5)_2$$

$$C_6H_5.CH(OC_2H_5)_2 + H_2O + HCl = = 2C_2H_5OH + HCl + C_6H_5.CHO.$$

After Grignard had shown that secondary alcohols are formed from magnesium organic compounds (2 mols.) and formic esters (1 mol.), Gattermann and Maffezzoli (*Ber.*, 1903, xxxvi., 4152; compare Farbenfabriken vorm F. Bayer and Co., D.R.P., 1904, 157573) obtained aldehydes from magnesium organic compounds (1 mol.) and formic esters 3 mols.); secondary alcohols are formed at the same time, and the yields of aldehydes are not particularly good. The formation of *o*-toluyl aldehyde from *o*-bromotoluene is represented as follows :—

$$CH_3.C_6H_4.MgBr + H.COOC_2H_5 = = BrMg.OC_2H_5 + CH_3.C_6H_4.CHO.$$

Gattermann (*Annalen*, 1906, cccxlvii., 347; compare Monier Williams, *Trans.*, 1906, lxxxix., 273) shows that ethoxymethyleneaniline may be used in place of ethyl formate; anils are then formed from which aldehydes are obtained by the action of mineral acids, thus—

$$C_6H_5.N:CH.OC_2H_5 + RMgBr = = C_6H_5.N:CHR + C_2H_5OMgBr$$

$$C_6H_5.N:CHR + H_2O = R.CHO + C_6H_5.NH_2.$$

Sachs and Loevy (*Ber.*, 1904, xxxvii., 874) find that additive compounds are formed from *iso*nitriles, for which Nef's formulation, R.N:C, is taken. These additive compounds, $R.N:C<^{Aryl}_{Mg.Br}$, when treated with mineral acids probably give first aldehydeimide derivatives, R.N:CH.Aryl, and then aldehydes, O:CH.Aryl. The method, however, is not a very practical one.

Ethers.

Klages (*Ber.*, 1904, xxxvii., 3987) has prepared a number of phenol ethers from aldehydes; for example, *o*-propenyl phenetole, $C_2H_5.O.C_6H_4.CH:CH.CH_3$, from ethyl salicylaldehyde and magnesium ethyl iodide.

According to Hamonet (*Comptes Rendus*, 1904, cxxxviii., 813, 975; 1904, cxxxix., 59), halogen-substituted methyl ethers interact with magnesium organic compounds, thus : $RMgX + XCH_2OR = MgX_2 + R.CH_2OR$.

* A Paper read before the British Association (Section B), Leicester Meeting, 1907.

Esters.

According to Grignard (*Comptes Rendus*, 1902, cxxxiv., 849), monoethyl ethylacetoacetate interacts with magnesium methyl iodide, partly in accordance with its ketonic structure, $CH_3.CO.CH(C_2H_5).COOC_2H_5$, to give the ester $(CH_3)_2C(OH).CH(C_2H_5).COOC_2H_5$.

Ethyl chlorocarbonate can be converted into ethyl benzoate by means of magnesium phenyl bromide when care is taken to avoid an excess of the latter by dropping it into an excess of the chlorocarbonate, thus : $C_6H_5MgBr + Cl.CO_2C_2H_5 = C_6H_5.COOC_2H_5 + MgClBr$ (Houben, *Ber.*, 1903, xxxvi., 3087). The reaction appears to be a general one.

Ethyl benzoate may also be prepared from magnesium phenyl bromide by a method described by Tschitschibabin (*Ber.*, 1905, xxxviii., 561), who uses normal carbonic esters :—

$$RMgX + CO(OC_2H_5)_2 = RC(OMgX)(OC_2H_5)_2$$

$$RC(OMgX)(OC_2H_5)_2 + H_2O = = R.COOC_2H_5 + C_2H_5OH + MgXOH.$$

If the reaction between magnesium organic compounds and orthocarbonic esters is moderated and not too prolonged it proceeds thus :—

$$C(OC_2H_5)_4 + RMgX = R.C(OC_2H_5)_3 + MgX(OC_2H_5).$$

Houben describes a method for the preparation of esters from alcohols or phenols (D.R.P., 1905, 162863; *Ber.*, 1906, xxxix., 1736). The alcohol or phenol is converted, by means of magnesium alkyl chloride, into its magnesium chloro-compound, which is then caused to interact with an acid chloride or anhydride, *e.g.*, with benzyl alcohol :—

$$C_6H_5.CH_2OH + C_2H_5MgCl = C_6H_5CH_2OMgCl + C_2H_6$$

$$C_6H_5CH_2OMgCl + (CH_3CO)_2O = = C_6H_5CH_2OCOCH_3 + CH_3.COOMgCl.$$

The preparation of the acetates of terpineol, linalool, thymol, and *cis*-terpin is described. The method gives excellent yields, and appears to be particularly suitable for the preparation of esters from unstable tertiary alcohols.

Nitrogen Compounds.

In continuation of his work on the formation of ketones from nitriles, Blaise (*Comptes Rendus*, 1901, cxxxii., 38, 478, 978) describes the preparation of anilides from phenyl *iso*cyanate, thus :—

$$C_6H_5.N:C:O + RMgI = C_6H_5.N:C<^{OMgI}_{R} \rightarrow$$

$$\rightarrow C_6H_5.N:C<^{OH}_{R} \rightarrow C_6H_5NH.COR.$$

Another method of obtaining anilides is given by Bodroux (*Comptes Rendus*, 1904, cxxxviii., 1427), who uses the magnesium organic compounds of primary aromatic amines. This type, RNHMgI, is obtained either by adding the amine to a cold ethereal solution of magnesium methyl iodide, or by the action of equimolecular amounts of methyl iodide and amine on magnesium in the presence of ether. When an ester of a monobasic acid is then added, and the product decomposed as usual by dilute acid, an almost theoretical yield of anilide is obtained :—

$$2RNHMgI + R'.COOR'' = MgIOR'' + R'.C(NHR)_2.OMgI,$$

$$R'.C(NHR)_2.OMgI + HCl = = R.NH_2 + MgICl + R'.CO.NHR.$$

The action of magnesium organic compounds on mustard oils is analogous to the action on *iso*cyanates. Sachs and Loevy (*Ber.*, 1903, xxxvi., 585; 1904, xxxvii., 874) obtained a number of thioanilides according to the scheme—

$$R.N:C:S + R'MgI = R.N:C(R').S.MgI$$

$$R.N:C(R').S.MgI + HCl = R.NH.CSR' + MgClI.$$

Nitrosohydroxylamines are formed by the action of nitric oxide on the Grignard reagent, nitrosophenylhydroxylamine being formed, for example, in good yield from magnesium

phenyl bromide (Sand and Singer, *Ber.*, 1902, xxxv., 3186; *Annalen*, 1903, cccxxix., 190):—

$$NO \rightarrow O{:}N.N{:}O \rightarrow O{:}N.N{<}\begin{matrix}OMgBr\\C_6H_5\end{matrix} \rightarrow O{:}N.N{<}\begin{matrix}OH\\C_6H_5\end{matrix}.$$

Since carbon dioxide and sulphur dioxide form carboxylic and sulphinic acids respectively with a Grignard reagent, Wieland (*Ber.*, 1903, xxxvi., 2315) tried the action of nitrogen peroxide in the expectation of obtaining acids of the type R.NOOH. Instead of this type, however, he obtained, in the aliphatic series, $\beta\beta$-dialkylated hydroxylamines, $R_2N.OH$, the nitrogen peroxide undergoing reduction. The preparation of $\beta\beta$-diethylhydroxylamine is described. Negative results were obtained in the aromatic series (Wieland and Gambarjan, *Ber.*, 1906, xxxix., 1499).

The action of magnesium phenyl bromide on β-phenylhydroxylamine has been investigated by Busch and Hobein (*Ber.*, 1907, xl., 2099), who obtain a 20 per cent yield of triphenylhydrazine. Possibly azobenzene is formed as an intermediate product, and then interacts thus:—

$$C_6H_5.N{:}N.C_6H_5 + C_6H_5MgBr = \begin{matrix}C_6H_5\\C_6H_5\end{matrix}{>}N{-}N{<}\begin{matrix}C_6H_5\\MgBr\end{matrix}.$$

An alternative explanation is suggested as more probable. Phenylhydroxylamine is partially converted into diphenylamine, which then condenses with phenylhydroxylamine: $(C_6H_5)_2NH + OH.NHC_6H_5 = (C_6H_5)_2N.NHC_6H_5 + H_2O$.

It might be noted here that magnesium organic compounds sometimes exhibit a reducing action. Franzen and Deibel (*Ber.*, 1905, xxxviii., 2716), for example, show that hydrazobenzene may be obtained in good yield from azobenzene and magnesium ethyl bromide:—

$$\begin{matrix}C_6H_5.N\\ \|\\ C_6H_5.N\end{matrix} + 2Mg{<}\begin{matrix}C_2H_5\\Br\end{matrix} = \begin{matrix}C_6H_5.N.MgBr\\ |\\ C_6H_5.N.MgBr\end{matrix} + C_4H_{10}$$

$$\begin{matrix}C_6H_5.N.MgBr\\ |\\ C_6H_5.N.MgBr\end{matrix} + 2H_2O = \begin{matrix}C_6H_5.NH\\ |\\ C_6H_5.NH\end{matrix} + 2MgBr(OH).$$

The action of the Grignard reagent on nitro-compounds has not been very thoroughly investigated. Moureu (*Comptes Rendus*, 1901, cxxxii., 837) obtained diethylhydroxylamine by the action of magnesium ethyl iodide on nitroethane and amylnitrite respectively. One of the products resulting from the action of magnesium ethyl iodide on nitrobenzene is ethyl aniline (Oddo, *Atti R. Accad. Lincei*, 1904, [5], xiii., II., 220).

A method of obtaining secondary amines from alkylidene bases is described by Busch (*Ber.*, 1904, xxxvii., 2691; compare Busch and Rinck, *Ber.*, 1905 xxxviii., 1761); thus C-methyl benzylaniline is obtained from magnesium methyl iodide and benzylidene aniline:—

$$C_6H_5.N{:}CH.C_6H_5 + MgCH_3I = C_6H_5.N(MgI){-}CH(CH_3).C_6H_5$$

$$C_6H_5.N(MgI){-}CH(CH_3).C_6H_5 + H_2O =$$

$$= C_6H_5NH.CH(CH_3).C_6H_5 + MgIOH.$$

The action on oximes has been studied by Busch and Hobein (*Ber.*, 1907, xl., 2096), and takes place in accordance with the scheme—

$$R.CH{:}N.OH + 2R'MgX = \begin{matrix}R\\R'\end{matrix}{>}CH.N{<}\begin{matrix}R'\\MgX\end{matrix} + Mg{<}\begin{matrix}OH\\X\end{matrix}$$

$$\begin{matrix}R\\R'\end{matrix}{>}CH.N{<}\begin{matrix}R'\\MgX\end{matrix} + H_2O = \begin{matrix}R\\R'\end{matrix}{>}CH.NHR' + Mg{<}\begin{matrix}OH\\X\end{matrix}.$$

According to F. and L. Sachs, tertiary amines combine with magnesium organic compounds to form compounds which are insoluble in ether (*Ber.*, 1904, xxxvii., 3088; compare Oddo, *Atti R. Accad. Lincei*, 1904, [5], xiii., I., 100). The compound of quinoline and magnesium phenyl bromide is represented as $C_9H_7N.(MgBr)C_6H_5$.

Forster and Judd (*Trans. Chem. Soc.*, 1905, lxxxvii., 368), in studying the action of magnesium methyl iodide on α-cyanocamphor, found that about 80 per cent of the latter compound escaped attack by the reagent, whilst the remainder was converted into the imine $C_8H_{14}{<}\begin{matrix}CH.C(CH_3){:}NH\\ |\\ CO\end{matrix}$, which on hydrolysis gave acetylcamphor.

When normal ethyl carbonate is added to the magnesium compound of a primary aromatic amine, one obtains a monosubstituted urethane, thus:—

$$2C_6H_5NHMgI + CO(OC_2H_5)_2 =$$
$$= (C_6H_5.NH)_2C(OC_2H_5).OMgI + MgI(OC_2H_5)$$
$$(C_6H_5.NH)_2C(OC_2H_5).OMgI + H_2O =$$
$$= C_6H_5NH_2 + C_6H_5NH.COOC_2H_5.$$

(Bodroux, *Comptes Rendus*, 1905, clx., 1108).

The application of the Grignard reagent for the preparation of diazoamino-compounds have been the subject of a series of papers by Dimroth (*Ber.*, 1903, xxxvi., 909; 1905, xxxviii., 670; 1906, xxxix., 3905). These compounds are obtained from diazobenzeneimide according to the scheme—

$$C_6H_5.N{<}\begin{matrix}N\\ \|\\ N\end{matrix} + RMgX = C_6H_5.N(MgX).N{:}NR$$

$$C_6H_5.N(MgX).N{:}NR + H_2O = C_6H_5.NH.N{:}NR + MgXOH.$$

The method is particularly useful for the preparation of aliphatic or mixed aliphatic-aromatic diazoamino-compounds, for the preparation of which the older method of Griess is not available. Thus, phenylmethyltriazene, $CH_3.N_3H.C_6H_5$; benzylmethyltriazene, $CH_3.N_3H.CH_2C_6H_5$, &c., have been prepared. Diazoaminomethane, $CH_3.N{:}N.NH.CH_3$, was prepared from methylazide, $CH_3.N{<}\begin{matrix}N\\ \|\\ N\end{matrix}$, and magnesium methyl iodide, according to the scheme given above. The isolation of this interesting compound was accompanied with great difficulties, due, on the one hand, to its instability, and, on the other, to the ease with which it dissolves in all solvents tried.

Alkyl and Aryl Metallic Compounds.

Pfeiffer and Schnurmann (*Ber.*, 1904, xxxvii., 319, 1125, 4617, 4618, &c.) describe a method of preparing alkyl and aryl metallic compounds by interaction of metallic halides, and the Grignard reagent either at the ordinary temperature or at 100°. Tin tetraethyl, for example, is prepared from tin tetrabromide and magnesium ethyl bromide: $SnBr_4 + 4C_2H_5MgBr = Sn(C_2H_5)_4 + 4MgBr_2$. Other tin compounds, such as tin tetraphenyl, tin tribenzyl chloride, tin trimethyl iodide, &c., are also obtained by this method, which has also been applied for making lead compounds; for example, lead tetraphenyl is obtained from lead chloride: $2PbCl_2 + 4C_6H_5MgBr = Pb + Pb(C_6H_5)_4 + 4MgClBr$.

The method has been very extensively applied, more particularly by Pfeiffer, for the preparation of derivatives of other elements such as mercury, thallium, phosphorus, arsenic, antimony, bismuth, and platinum.

Kipping (*Trans. Chem. Soc.*, 1907, xci., 209, 717) has made a special study of silicon compounds, and by aid of the Grignard reaction has prepared *dl*-sulphobenzylethylpropyl silicyl oxide,—

$$SO_3H.C_6H_4.CH_2.\begin{matrix}C_2H_5\\ |\\ Si\\ |\\ C_3H_7\end{matrix}{-}O{-}\begin{matrix}C_2H_5\\ |\\ Si\\ |\\ C_3H_7\end{matrix}.CH_2.C_6H_4.SO_3H,$$

and obtained evidence of the resolution of this compound into optically active components. Incidental to this work a number of silicon compounds are described, such as phenylethylsilicon dichloride, $C_2H_5(C_6H_5)SiCl_2$; phenylethylpropylsilicyl chloride, $C_2H_5(C_3H_7)(C_6H_5)SiCl$; phenylbenzylethylpropylsilicane, $C_2H_5(C_3H_7)(C_6H_5)(C_7H_7)Si$; benzylethylsilicon dichloride, $C_2H_5(C_7H_7)SiCl_2$; benzylethylpropylsilicyl chloride, $C_7H_7(C_2H_5)(C_3H_7)SiCl$, &c.

(To be continued).

A REVISION OF THE ATOMIC WEIGHT OF POTASSIUM.*

II. The Analysis of Potassic Bromide.

By THEODORE WM. RICHARDS and EDWARD MUELLER.

(Concluded from p. 159).

The Drying and Weighing of Potassic Bromide.

For reasons already mentioned in the paper on potassic chloride, the salt under investigation must be fused before weighing. Unfortunately, potassic bromide when fused in air in a platinum vessel attacks the platinum to a considerable extent. Although it is shown later that this action does not seriously affect the weight of silver needed to precipitate the bromine in the salt, it was, nevertheless, desirable to avoid all such irregularities. No such action is observed when the fusion takes place in an atmosphere of pure dry nitrogen. Accordingly, in all work to be recounted, the potassic bromide was protected in this way during its fusion in a well-seasoned platinum boat, and was finally, by means of the Harvard "bottling apparatus," shut up in a tight weighing bottle in an atmosphere of pure dry air. The details have already been adequately given in several places, especially in the account of the recent work on the atomic weight of cæsium (Richards and Archibald, *Proc. Amer. Acad.*, 1903, xxxviii., 451; *Zeit. Anorg. Chem.*, 1903, xxxiv., 362). The only difference in the present procedure was demanded by the high fusing-point of potassic bromide (750°); on account of this, a porcelain ignition-tube was substituted for one of glass, as in the case of calcic chloride (Richards, *Journ. Am. Chem. Soc.*, 1902, xxiv., 374).

Even with all possible care, however, the platinum boat was distinctly attacked, almost always losing in weight during the fusion. In two of the cases—Analyses 1 and 14—where the potassic bromide was fused for some time in the boat, the corrosive action was very considerable, causing losses of weight of 0·0007 and 0·0014 grm. respectively. One would be disposed to reject these determinations entirely, except for the fact that their average result, $\frac{KBr}{Ag} = 1{\cdot}10317$, is almost exactly identical with that of the average of Results 5 and 6, in which the boat was scarcely attacked at all, namely, $\frac{KBr}{Ag} = 1{\cdot}10318$. Instead of being rejected, these results are therefore retained and used as evidence that even a considerable amount of dissolved platinum has no preceptible effect on the weight of silver precipitated by the salt. In a majority of the other cases, the change in weight of the boat during the fusion was less than 0·0001 grm. The average loss in Analyses 10, 11, 12, and 16, in which the argentic bromide was weighed, was less than 0·00009 grm.; hence, even if platinum had been present in the potassic bromide in a state of fine division it could not have exerted any essential effect upon the result of this series of analyses.

As a matter of fact, the potassic bromide always gave a perfectly clear aqueous solution except once, namely, in Analysis 14. In this case several small flakes of platinum were noticed in the salt both before and after the salt was dissolved in water.

The solutions were always perfectly neutral to phenolphthaleïn, a fact which is adequate proof of the retention of all the bromine during fusion, and also of the absence of oxalate from the potassic bromide crystals.

The third sample of potassic bromide had contained ammonic bromide, which was expelled during the fusion. During the expulsion of this salt, the boat was placed near the exit end of the porcelain tube, and there gradually heated to redness in a current of nitrogen. During the entire operation the middle portion of the porcelain tube was kept red-hot in order to prevent backward diffusion of the ammonic bromide, which by condensing might later cause a contamination of the potassic bromide. All the ammonic bromide having been sublimed, the boat was pushed into the middle of the tube, and the potassic bromide fused as described above. There being a possibility that even at the fusing-point of potassic bromide some ammonic bromide might still be retained, another portion of the same third sample of bromide was fused under approximately the same conditions as in the analyses. The solution of the bromide thus obtained was submitted to the Nessler test, being compared with a tube of pure water containing the same amount of reagent. No colour was visible in either tube, hence no appreciable amount of ammonic bromide remained to contaminate the potassium salt.

The salt thus prepared for analysis was weighed in its glass-stoppered weighing bottle by substitution, using as the substituting tare a precisely similar weighing bottle. Successive weighings of the same specimen were always practically identical. The balance and weights were similar to those used with sodic and potassic chlorides, and all the precautions were the same. At each weighing the heights of the barometer, the temperature of the balance-room, and the humidity as indicated by a hygrometer were recorded. The density of the displaced air could thus be determined for each case. The variations from the average were, however, not enough to affect essentially any of the results, as weighings were not made under any abnormal atmospheric conditions. The weights were of course standardised by the usual Harvard method.

The specific gravity of potassic bromide must be known to within five one-hundredths of a unit in order to correct the weighings to the vacuum standard with sufficient accuracy. Its determination has been undertaken with a variety of methods, with a variety of results, ranging from 2·20 to 2·756. (For the literature, see Meyerhoffer, "Landolt u. Börnstein"; "Physikalisch-Chemische Tabellen," 1905; and Clarke, "Constants of Nature," Part I., Macmillan, 1888). The more recent results all tend towards the highest value, found by Krichmeyer, 2·756 (*Zeit. Physikal. Chem.*, 1896, xxi., 81). This appeared to be the most probable, because the usual errors cause low results; but as this determination was made with only a single crystal, and as the salt weighed in the present research had been fused, it was thought best to investigate further. Accordingly, a pure sample of potassic bromide was further purified by being three times recrystallised with centrifugal draining, when it gave no flame test for sodium (see Krichmeyer's experience, *loc. cit.*). This product was fused in platinum and coarsely pulverised; its specific gravity was determined in an Ostwald pycnometer, modified for use with solids, using toluol as the fluid to be displaced. The toluol had been re-distilled, and possessed a density 0·8608 at 25°, referred to water at 4°; 8·2568 grms. of potassic bromide displaced 2·6009 grms. of the toluol at 25°, a result which indicates a density of 2·73. Time was lacking for a repetition of the experiment, but this preliminary result was enough to show that the fused salt is essentially in the same state as the crystallised salt. The difference between the two values is too small to affect the vacuum correction; the average value 2·74 was used.

The Precipitation and Weighing of Argentic Bromide.

In order to determine the weight of argentic bromide obtainable from the bromine in potassic bromide, the latter salt was precipitated by a very slight excess of argentic nitrate, both substances being dissolved in large quantities of the purest water. The method differed but slightly from that which had been used recently in so many other cases of the same kind. The argentic nitrate was prepared from a weighed amount of pure silver, but no attempt was made in this series to determine the exact amount of silver required, as it was desired not to complicate the process before weighing the argentic bromide. Care was taken to have an excess, but only a slight excess. The silver was dissolved in nitric acid with

* *Publication* No. 69, Carnegie Institution of Washington.

all the usual precautions, and the precipitation was carried out in orange-red light in the dark-room devoted to accurate work of this kind. The potassic bromide had been dissolved out of the boat by digestion in a large platinum dish, and been transferred to a 2 litre glass-stoppered Jena Erlenmeyer flask with careful rinsing, and every precaution to prevent any gain or loss. After being well shaken, the flask containing the silver bromide was allowed to stand until the mother-liquor had become clear. The solution was filtered through a platinum Gooch-Munroe crucible, and the precipitate was washed by decantation, first with an extremely dilute acid solution of silver nitrate, and finally with exceedingly dilute nitric acid to prevent colloidal solution. With this latter faintly acid liquid the precipitate was transferred to the crucible. The silver bromide was dried at least twelve hours in the filtering crucible at 130° in an electric oven, and weighed (Richards, *Am. Chem. Journ.*, 1899, xxii., 45). It was then fused in a porcelain crucible, in a furnace where it was effectively protected from flame gases, in order to determine the trace of moisture always retained. The wash-waters and the solution obtained on neutralising the ammoniacal rinsings of the flask gave no indication of the presence of bromine on careful testing in the nephelometer.

In using the Gooch-Munroe crucible, all the precautions pointed out in the preceding paper were carefully heeded. A perforated plate was always placed on top of the friable sponge to prevent rupture. After each determination any bromide clinging to it was leached out with potassic cyanide, which was then washed away with nitric acid, and finally very thoroughly with water. The solvent action of the cyanide occasionally loosened portions of the spongy film, but there was no difficulty in repairing the injury. Upon drying in the electric oven, the crucible was ready for another analysis.

In addition to the loss of weight on fusion, two other very small and somewhat uncertain corrections were applied to the weight of the argentic bromide, but because they were of about the same magnitude and of opposite sign, their effect was practically negligible. These were a correction for platinum corroded from the boat during the fusion of potassic bromide, and a correction for argentic bromide dissolved in the water used for washing. Because these corrections have not been considered in most work of this kind, a word about them may not be amiss.

In the series under discussion the average loss of the boat in each determination was less than 0·00009 grm. All of this trace of platinum may have been present as invisible dust in the solution, and thus may have been weighed with the argentic bromide, or all of it may have been in a soluble form and may have remained in solution. Because of this uncertainty, a compromise was made, and half of the loss of weight of the boat (in the mean 0·00004 grm.) was subtracted from each weight of argentic bromide. As the average total weight of argentic bromide was over 4 grms., this compromise could not have introduced an error as great as 1 part in 100,000 in either direction.

According to Stas (" Œuvres," I., 89), argentic bromide is wholly insoluble in water, but recent experiments show that in the flocculent form it is unquestionably soluble to a slight extent (Böttger, *Zeit. Phys. Chem.*, 1903, xlvi., 602; Kohlrausch and Rose, *Zeit. Phys. Chem.*, 1893, 12, 234; also Richards, *Proc. Amer. Acad.*, 1894, xxx., 385). As in the case of the chloride, its solubility is greatly diminished by the addition of an excess of either precipitant; but whether or not any is dissolved by a very dilute acid solution of argentic nitrate, such as that used in washing, it is practically impossible to discover. It is not unlikely, however, that about as much was dissolved by this solution as by the dilute hydrobromic acid used by Baxter in his admirable work on the atomic weight of bromine (*Journ. Am. Chem. Soc.*, 1906, xxviii., 1322); and in this solution it is easy to find the amount of dissolved substance. Baxter found, as a matter of fact, in his last seven most exact syntheses an average of 0·00004 grm. of argentic bromide in each of the wash-waters—a figure which was added to each of our weights of argentic bromide, because the other circumstances of the analysis were similar in the two cases. On the average, this correction exactly eliminates the other, and except for the sake of completeness, they might both have been wholly neglected.

Of course, all the weighings were corrected to the vacuum standard, by adding 0·000041 grm. to every apparent grm. of argentic bromide and 0·00029 grm. to every apparent grm. of potassic bromide, as calculated from the figures 6·473, 2·74, and 8·30, for the densities of argentic bromide (Baxter and Hines, *Am. Chem. Journ.*, 1904, xxxi., 220), potassic bromide, and the brass weights respectively. All the determinations made are given in the table below.

The Ratio of Argentic Bromide to Potassic Bromide.

Experiment No.	Weight of KBr in vacuum. Grms.	Corrected wt. of AgBr in vacuum. Grms.	Parts of KBr for 100·00 parts of AgBr.	At. wt. of potassium Br=79·953.
10.	2·19027	3·45617	63·3728	39·114
11.	4·19705	6·62285	63·3723	39·113
12.	2·06723	3·26206	63·3719	39·112
16.	2·58494	4·07889	63·3736	39·115
Total average	11·0395	17·41997	63·3727	39·1135
Probable error			0·0003	0·0004

The extreme deviation from the mean corresponds to an error of weighing the potassic bromide of 0·00004 grm., a reasonable quantity. The " probable error " indicates that there is but little chance that the atomic weight of potassium is much below 39·113 or much above 39·114, if constant chemical errors were successfully excluded. Stas found in a single experiment the number 63·383 instead of 63·373 (" Untersuchungen," *Trans. Aronstein*, 1867, p. 340).

With unlimited time more determinations might well have been made, but the agreement of these four results is so good that further repetition seemed to be not very urgent.

The Determination of the Silver needed for Precipitation.

The silver titration method of Guy-Lussac, as developed by Pelouze, Mulder, Stas, and more especially by the recent work at Harvard, yields very consistent and accurate results, if the proper conditions are carefully observed. The reading of the end-point is rendered easy by the use of the nephelometer (Richards and Wells, *Am. Chem. Journ.* 1904, xxxi., 235). In the case of the somewhat soluble chloride, various precautions must be strictly heeded; but with argentic bromide, which is almost insoluble, the matter is a simpler one, and a very slight excess of either bromide or silver can be easily determined.

The method used in the present case is easily inferred from previous Harvard work of the same kind. From the weight of a piece of the purest silver, the equivalent amount of potassic bromide was calculated; slightly more than this amount of substance was then fused as before in a platinum-iridium boat placed in the porcelain tube of the bottling apparatus. From the weight of fused bromide, the equivalent quantity of silver was calculated; the greater part of the difference between this calculated weight and that of the original piece of silver was added in the shape of pure silver wire (Richards and Parker, *Proc. Amer. Acad.*, 1896, xxxii., 60), and any final difference of 0·1 or 0·2 mgrm. was made up with a dilute solution of silver nitrate. The silver was dissolved in nitric acid, and the nitrous acid expelled as usual, and the solution was then diluted to about tenth normal.

To the dilute bromide solution, with continual agitation, was added this dilute argentic solution; the total volume, including the water used in rinsing, usually amounted to about 1·5 litres. After shaking steadily for fifteen minutes, and occasionally for a day, the mixture was allowed to

settle during another day. When clear above, about 0·05 litre of the aqueous solution was withdrawn and tested in the nephelometer, one tube being treated with an excess of bromide, the other with an excess of argentic nitrate. If any difference in the opalescence was noticeable after due time had been allowed for the very faint clouds to attain their maxima, the slight deficiency was made up in the flask by means of solutions containing approximately 1 mgrm. of argentic nitrate or of potassic bromide per millilitre. These additions were continued till equality in the opalescence was attained. From the sum of the original weights and subsequent additions, the total amounts of bromide and silver were obtained; from these, reduced to vacuum, the ratio was calculated. All the analyses which were performed are given in the table, excepting No. 2, which was rejected for just cause before it was finished. Vacuum corrections of +0·00029 for every grm. of potassic bromide and −0·00003 for every apparent grm. of silver were applied. Most of these experiments were made before those given in the preceding table, a fact which may account for the slightly less satisfactory agreement of the individual results. Because the deviations could not be traced to any definite cause of disturbance, they must be ascribed to accident.

The Ratio of Potassic Bromide to Silver.

Experiment No.	Weight of KBr in vacuum. Grms.	Weight of silver in vacuum. Grms.	Parts of KBr corresponding to 100·00 parts Ag.	Atomic weight of potassium if Br=79·953.
1.	4·33730	3·93164	110·318	39·113
3.	4·18763	3·79587	110·320	39·115
4.	4·15849	3·76943	110·321	39·116
5.	3·67867	3·33450	110·321	39·116
6.	3·60484	3·26776	110·315	39·110
7.	4·78120	4·33387	110·322	39·118
8.	5·67997	5·14860	110·321	39·116
9.	6·41587	5·81571	110·320	39·115
13.	2·88134	2·61184	110·318	39·113
14.	3·64383	3·30309	110·316	39·111
15.	3·12757	2·83504	110·318	39·113
	Total average		110·3190	(*a*) 39·1143
	Probable error		0·0004	0·0004

(*a*) The average 39·1143 is calculated from the average 110·3190, not from the average of the individual values of the atomic weights in the column above. The difference of course is very slight.

The "probable error" is as small as before because of the greater number of determinations, and the mean deviation from the average value is only one in the last decimal place. It will be observed that these results point to the limits 39·113 and 39·115 as the extreme values between which the atomic weight of potassium must fall, in essential agreement with the previous results.

Marignac's seven experiments on this ratio give values ranging from 110·303 to 110·369, while Stas's fourteen results ranged from 110·332 to 110·361.

Obviously the results furnish a means of calculating the atomic weight of bromine, when taken in connection with the foregoing series, entirely independent of any other work. Thus, Br = (110·319/63·3727—1·00000) 107·93 = 79·954, a value almost identical with Baxter's value, 79·953. This is excellent proof that the bromine used in the present research was pure, and that the occlusion of electrolytes by argentic bromide was small.

The Atomic Weight of Potassium.

The preceding paper and the present one together yield four ratios determined with modern precision, which together fix the atomic weight of potassium as definitely as could be expected. The respective values are as follows:—

	K=
From the ratio of argentic to potassic chloride	39·1134
From the ratio of metallic silver to potassic chloride	39·1145
From the ratio of argentic to potassic bromide	39·1135
From the ratio of metallic silver to potassic bromide	39·1143
Average atomic weight of potassium if Ag = 107·930	39·1139

These figures are interesting and significant. The maximum departure from the mean is only 1 part in 70,000, and such differences as exist in the figures are explicable. It is likely that the slightly lower value given by the first member of each pair of series was due to a trace of occlusion of potassic nitrate by each of the precipitates—a circumstance which cannot be absolutely prevented. Therefore the higher values, averaging 39·1144, are more probable. The differences are, however, wholly negligible at present.

In this connection it is interesting to note that Clarke in 1897, from a miscellaneous collection of partly uncertain results obtained by others, decided upon the almost identical value, 39·112 ("Re-calculations," p. 57), although at the same time from similar results he obtained values much too low for chlorine and iodine, somewhat too low for bromine, and much too high for sodium.

The very close mutual agreement of the new results obtained from two different compounds is a satisfactory verification of the relative values yielded by the recent work on the atomic weights of chlorine and bromine (Richards and Wells, *loc. cit.*; Richards, *Trans. Am. Phil. Soc.*, 1904, xliii., 116; Baxter, *loc. cit.*). The value of chlorine found from the work on potassium chloride was 35·475, and that of bromine from the present work is 79·954. The ratio of chlorine to bromine is thus found to be 0·44369, whereas the ratio computed from the work of Richards and Wells, and of Baxter, is 0·44367.

Against such an accumulation of concordant data as that just presented, the older figures can have no important weight. Whatever may have been the cause of the irregularity and internal inconsistency of Stas's results with potassic chloride and bromide, there seems to be little reason to doubt that the outcome of the present investigation, 39·114, really represents the atomic weight of potassium.

It is needless to point out that this change in the atomic weight of potassium will affect many other atomic weights.

Summary.

This investigation upon the atomic weight of potassium presents, among other considerations, the following additions to the knowledge of the subject:—

1. The problem of preparing pure potassic bromide was solved in two ways.

2. An unusually satisfactory method for preparing pure potassium hydroxide was developed. This method is applicable to other alkalis, and will be described elsewhere in greater detail.

3. The ratio of silver to potassic bromide was re-determined, and found to be 100·000 : 110·319. The atomic weight of potassium was thus found to be 39·1143, if silver is 107·930 and bromine 79·953.

4. The ratio of argentic bromide to potassic bromide was found to be 100·000 : 63·373. This determination yielded an essentially equal value, K = 39·1135.

5. These values confirm in a striking manner the simultaneously executed work upon potassic chloride, and unite with them in showing that the atomic weight of potassium is 39·114.

6. By thus agreeing, these four values support the new value for the atomic weight of chlorine in relation to silver and bromine.

Radio-activity of Uranyl Molybdate.—B. Szilard.—The author has prepared uranyl molybdate by the same process as Lancien, in order to examine the truth of the latter's statement as to its abnormally high activity. He finds, however, that the radio-activity is absolutely normal and proportional to the amount of uranium present.—*Comptes Rendus*, cxlv., No. 10.

NOTICES OF BOOKS.

The Principles and Practice of Brewing. By WALTER J. SYKES, M.D., D.P.H., F.I.C. Third Edition, thoroughly Revised by the Author and ARTHUR R. LING, F.I.C. London: Charles Griffin and Co., Ltd. 1907.

THIS valuable treatise combines a text-book of the theory of brewing, dealing with the physics, chemistry, and biology of the subject, with a practical laboratory guide in which a systematic course of the experimental work necessary for a thorough study of brewing and malting is given. It is clearly and authoritatively written, and no better recommendation can be urged than the fact that it has reached its third edition in less than ten years. The text had been revised, with the co-operation of Mr. Ling, by Dr. Sykes before his death in December last year, and the work has been brought thoroughly up-to-date; the new edition contains important additions on thesubject of stereochemistry, and the chemistry of the carbohydrates and the enzymes, while other parts of the book have also been considerably enlarged.

Recent Improvements in Methods for the Biological Treatment of Sewage. By W. J. DIBDIN, F.I.C., F.C.S. Second Edition. London: Sanitary Publishing Company.

THIS book contains a description of the author's Multiple Surface Biological Beds, for dealing with suspended matters with aërobic action throughout, which have been used in different localities with exceedingly satisfactory results, and it further gives a condensed account of modern methods of sewage treatment. It treats more especially of biological processes in which no chemical agents are employed, and the statistics quoted show that the double contact bed system, with slate as the filling for the primary beds, is not to be surpassed for simplicity and economy. The book may be regarded as a supplement to the third edition of the author's well-known treatise on "The Purification of Sewage and Water," giving details of researches and experiments performed since its publication.

The Dispensatory of the United States of America. By Dr. GEO. B. WOOD and Dr. FRANKLIN BACHE. Nineteenth Edition, by H. C. WOOD, M.D., LL.D., JOSEPH P. REMINGTON, Ph.M., F.C.S., and SAMUEL P. SADTLER, Ph.D., LL.D. Philadelphia and London: J. B. Lippincott Company.

THE Food and Drugs Act, with Rules and Regulations, of the United States Government is printed in full in this Dispensatory, which will be found invaluable by druggists and pharmacists. An abstract of the national formulary is included, and as in the earlier editions the official and unofficial preparations both of the United States and British Pharmacopœias are separated. In Part III. the tests and test solutions for determining the purity and strength of many important chemicals are given, and fuller references are now added to chemical, pharmaceutical, and therapeutical literature. Thus the Nineteenth Edition represents a decided advance upon the earlier volumes of the Dispensatory, and it is clear that every endeavour has been made to render it fuller and more convenient in use than its predecessors.

The Electric Furnace in Iron and Steel Production. By JOHN B. C. KERSHAW, F.I.C. London: The Electrician Printing and Publishing Company, Ltd. 1907.

THIS book is based upon a series of papers contributed by the author to the *Iron Trade Review*, of Cleveland, U.S.A., last year, and afterwards published in *The Electrician*. In them the author considered in detail the four chief types of furnaces and processes—those of Heroult, Keller. Kjellin, and Stassano—which have been subjected to lengthy trials upon an industrial scale, and also discussed shortly some methods which have not been so long before the public, and which can hardly be said to have passed the experimental stage. Although it is undeniable that all electric smelting processes appear to be utterly unable to compete with blast-furnace processes at present, except possibly under peculiarly favourable combinations of circumstances, there seems to be much more likelihood that electric refining methods will begin to be widely used with financially satisfactory results, and the book gives a useful summary of the present state of affairs; the author has endeavoured to sift out from the great number of figures relating to yields and costs, which have appeared in various periodicals, those which are based upon actual experimental results and not upon estimated expenses, and the chapter upon this subject is well worth the careful consideration of engineers.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlv., No. 9, August 26, 1907.

Propylene Oxide, $H_3C{-}CH{-}CH_2$ (O bridging CH and CH_2).—Louis Henry.—When an ethereal solution of propylene oxide acts upon ethyl magnesium bromide, also dissolved in ether, an alcoholic liquid is obtained boiling at 115—120°. This may be either $CH_3{-}CH(OH){-}CH_2{-}CH_2{-}CH_3$ (boiling-point 118°) or $CH_3{-}CH_2{-}CH(OH){-}CH_2{-}CH_3$ (boiling-point 116°). These two alcohols may be differentiated by converting them into semicarbazones. The semicarbazone of methyl propyl ketone, $H_3C{-}CH_2{-}CH_2{>}C{=}N{-}NH{-}CO(NH_2)$, fuses at 100°, while that of the symmetric diethyl ketone, $H_3C{-}CH_2{>}C{=}N{-}NH.CO(NH_2)$, fuses at 138°. By this method it may be shown that the alcohol is normal methyl propyl carbinol, $CH_3{-}CH(OH){-}CH_2{-}CH_2{-}CH_3$. Thus propylene oxide behaves towards magnesium derivatives in the same way as ethylene oxide.

No. 10, September 2, 1907.

Action of Gravity on the Deposit of Induced Radio-activity. — Mdme. Curie. — Some years ago, P. Curie observed that when radium emanation is contained in a closed vessel the interior of which is covered with phosphorescent zinc sulphide, the luminosity of this substance under the action of the emanation is gradually concentrated in the regions round the bottom. When the vessel is turned upside down, so that the luminous part is at the top, the luminosity of the upper part gradually disappears, while a new luminous region is formed below. The position of the region appears to be independent of the neighbourhood of magnets and of the temperature. The experiments of P. Curie and Debierne have shown that a metal sheet placed in a closed vessel which contains some emanation becomes more active the greater the free space in front of the sheet. When two parallel sheets are placed face to face, if their area is large compared with their distance apart, the activity acquired by the opposite faces increases with the distance. The author has placed in a vessel containing emanation pairs of parallel sheets, all at the same distance, some horizontal and others vertical, the exterior faces being protected, so that only the faces turned towards one another could become active. When the plates were exposed to the action of the emanation for two or three days, the emanation was drawn off and the intensity of the radio-activity of the active faces of different sheets determined. It was found that all the vertical sheets, and all the horizontal ones turned downwards, have the same activity for equal surfaces, while the horizontal sheets turned upwards have

an activity from two to five times as great. Hence the induced radio-activity suspended in the gas which surrounds the sheets behaves like a heavy substance, and falls downwards. The presence of water is necessary for the production of the phenomenon, and when the air in the vessel is quite dry the phenomenon does not occur. The intensity of the phenomenon seems to depend upon the concentration of the emanation. It depends also upon the distance of the sheets, and increases with it up to a certain limit. The phenomenon does not occur at very small distances (2 mm.).

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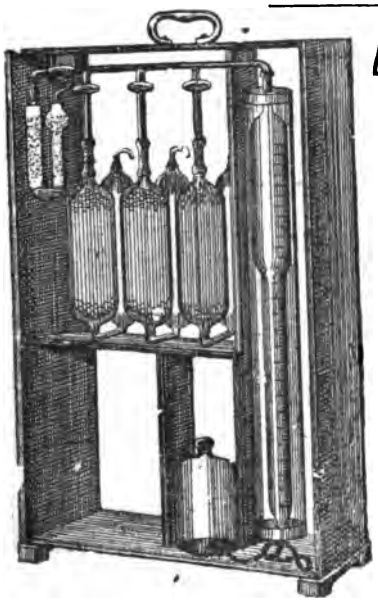

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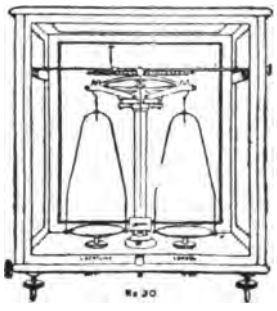

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RESEARCHES ON THE DENSITIES OF GASES.

By PHILIPPE A. GUYE.

The researches described in this paper were carried out during the past three years in the Laboratory of Physical Chemistry of the University of Geneva, in collaboration with MM. Jaquerod, Pintza, Davila, Gazarian, and Baume. The aim of the experiments was to determine with as great a degree of accuracy as possible the molecular weights of the gases in order to provide a control for the atomic weights. Two methods of determining the densities were employed—Regnault's bulb method and the volumeter method. In the former, Regnault's directions were followed closely, small bulbs of capacities 0·8 and 0·4 litre being used. Contrary to expectation it was found that the results with small bulbs agreed amongst themselves quite as well as those obtained in experiments with much larger bulbs, probably because errors arising from accidental causes connected more especially with the surface were minimised. The only objection to the use of small bulbs is the fact that possibly condensation may occur on the inner wall, especially in the case of hygroscopic gases; it is essential to rinse the bulbs not only with air dried over phosphorus pentoxide, but also with the thoroughly dried gas which is being examined. Each operation must be followed by complete evacuation, and the air must not be allowed to enter the bulb between the determinations. The volumeter method, first employed by Morley to determine the density of hydrogen, may be carried out in two ways. The gas may be set free from an apparatus which can be weighed, and which is constructed in such a way that the gas can come out only in a perfectly pure dry state. The gas then passes into a series of one or more graduated bulbs kept at 0°, and exhausted by a mercury pump. The pressure is measured either with a special manometer or else by means of a barometer. Then, since the temperature, pressure, capacity of the bulbs, and loss of weight of the generating apparatus are known, the density can be calculated. In the second method the volumeter after being exhausted is filled with the gas in as pure a state as possible, and kept at 0° in ice; the exact pressure of the gas is noted. Then it is absorbed in an appropriate apparatus, previously weighed. The volumeter method does not need correction for the contraction of the bulbs; it is only necessary to reduce the weight found to the weight *in vacuo*, for a counterpoise made of the same glass and having the same weight as the generating or absorbing apparatus is used. Whatever method is employed the correction for the compressibility of the gas can generally be neglected, when the pressure differs from 760 mm. by only a few mm.

Choice of a Unit.—It is absolutely indispensable to choose a common unit, and it is found most convenient to express all the results in terms of the weight of the normal litre of the gas, *i.e.*, at 0° C., under a pressure of 760 mm., at sea level and in latitude 45°.

Choice of Definite Values.—When making a choice between different numbers obtained for the density of each gas, the following points have been taken into consideration:—1. The nature of the methods employed for preparing and purifying the gas. Concordant results obtained with the same gas prepared in two or three different ways are always regarded as the most reliable. 2. Degree of agreement of the mean values of the same gas as determined by different observers. When the mean values of two observers agree, but differ from that of a third, the latter is, generally speaking, ignored.

Discussion of the Results.

Oxygen.—Morley performed forty-one determinations of the density of oxygen under very different conditions; these give as the mean value of the weight of the normal litre 1·42900 grm. Rayleigh used oxygen prepared by three different methods, and obtained the number 1·42905 grms. Other results are given, with the experimenters' names, in the following table:—

	Grms.
Morley	1·42900
Rayleigh	1·42905
Gray	1·22896 (*a*)
Leduc	1·4288
Jaquerod and Pintza	1·4292
Mean	1·4290

(*a*) As printed; evidently should be 1·42896.—*Ed.* C.N.

Thus, the value 1·42900 grms. for the weight of the normal litre is certainly accurate to within 1/10000 and probably within 1/20000.

Nitric Oxide, NO.—Gray was the first to determine accurately the density of this gas. He prepared it by the action of acetic acid on sodium nitrite and potassium ferrocyanide; then washed with caustic potash, dried over phosphorus pentoxide, liquefied, and fractionated at a low temperature. The results obtained agreed remarkably well among themselves, and also with those of Guye and Davila, the mean value being 1·3402 grms.

Carbon Dioxide, CO_2.—The mean values of the results obtained by Rayleigh, Leduc, and Guye and Pintza are 1·9769, 1·9763, and 1·9768 respectively. The last is probably the most correct.

Nitrous Oxide, N_2O.—Leduc found 1·9780, using the commercial liquefied gas. Rayleigh in two separate series of experiments, using gas prepared by different methods, found 1·9777, while Guye and Pintza, obtaining the gas by the double decomposition of sodium nitrite and hydroxylamine sulphate, found 1·9774. Taking into account the fact that possibly by the last method the gas is not obtained absolutely free from air, it appears probable that the last number is low, and the value adopted is Rayleigh's, viz., 1·9777, which is also the mean of Leduc's, Guye and Pintza's, and Rayleigh's.

Hydrochloric Acid, HCl.—The mean of numbers obtained by Guye and Gazarian, and Gray, is 1·6398, which may be adopted provisionally; new determinations are, however, being carried out.

Ammonia, NH_3.—Leduc found 0·7719 grm., which, however, must be rejected because it is affected by an error due to the presence of organic bases. Guye and Pintza obtained 0·7708, and Perman and Davies 0·77085. The former may be accepted as correct.

Sulphurous Anhydride, SO_2.—The value 2·9266 has been found by Jaquerod and Pintza, Leduc and Baume.

The accompanying table gives a summary of these results. Column I. gives the values found by Leduc, Column II. those of Rayleigh, In Column III. the results of different observers are given (Morley, Ramsay, Gray, Perman, and Davies), and in Column IV. the figures obtained in the author's laboratory in Geneva. Column V. gives those numbers which in the author's opinion are probably correct, and in Column VI. the ratios to the densities of oxygen are tabulated.

The following general conclusions can be drawn from the work carried out in the author's laboratory in Geneva during the last three years:—

1. Methods of determining the densities of gases in the hands of different experimenters give results which agree generally to within 1/10,000 at least, when the mean of six experiments, which do not differ among themselves by more than 3/10,000 or even 5/10,000, is taken.

2. This agreement can be obtained with gases which are very difficult to dry and purify, such as ammonia, sulphurous anhydride, hydrochloric acid, and nitric oxide. The bulbs must be thoroughly dried with dry air, and then

Weight of Normal Litre, in Grms. ($t=0°$, H=760, $h=0$, $\lambda=45°$).

Gas.	I. Leduc.	II. Rayleigh.	III. (Various).	IV. Guye's laboratory.	V. Values accepted.	VI. Densities referred to O_2.
O_2	(1·4288)	1·42905	1·42900 M. 1·42896 Gr.	(1·4292) J. P.	1·42900	1·00000
H_2	0·8982	(0·08998)	0·089873 M.		0·08987	0·062890
N_2	1·2503	1·2507	1·2507 Gr.		1·2507	0·87523
CO	1·2501	1·2504			1·2504	0·87502
NO	(1·3429)		1·3402 Gr.	1·3402 G. D.	1·3402	0·93786
Ar		1·7809	1·7808 R.			1·2463
CO_2	1·9763	1·9769		1·9789 G. P.	1·9768	1·3833
N_2O	1·9780	1·9777		1·9774 G. P.	1·9777	1·5840 (*a*)
HCl	(1·6407)		1·6397 Gr.	1·6398 G. G.	1·6398	1·1475
NH_3	(0·7719)		0·77085 P. D.	0·7708 G. P.	0·7708	0·53940
SO_2	2·9266			2·9266 J. P. 2·9266 B.	2·9266	2·0480
Air	1·2927	1·2928			1·2928	0·90469

(*a*) As printed; evidently should be 1·3840.—*Ed.* C.N.

rinsed with the perfectly dry gas. If this is done, no appreciable differences are found between the values obtained with 3·5 litre bulbs and with those holding only 0·5 litre.

3. The experimenter must pay special attention to the purification of the gas. Processes based upon the liquefaction of the gas, followed by rectification at low temperatures, are specially recommended.

4. It is preferable to calculate directly the weight of the normal litre of the gas, rather than to refer the densities to those of a standard gas, *e.g.*, oxygen or air.—Abstracted from the *Archives des Sciences Physiques et Naturelles*, xxiv., p. 34.

OBSERVATIONS AND DEDUCTIONS OBTAINED FROM A CONSIDERATION OF THE NUMBERS GIVEN FOR THE ATOMIC WEIGHTS OF THE ELEMENTS BY THE INTERNATIONAL COMMITTEE (1905) WHICH LEAD TO A RATIONAL DETERMINATION OF THE CONSTITUTION AND STRUCTURE OF EACH ELEMENT.

By HAWKSWORTH COLLINS, B.A. (Camb.).

1. THE first observation, which is not original, was made several years ago, viz., that the numbers obtained for the atomic weights of many elements approximate to whole numbers. In an investigation with regard to the constitution and structure of elements, this observation is too patent to be ignored.

(A). The first deduction, which is of course, not original, is that the elements are multiples of the element hydrogen.

2. The second observation is entirely original, as are all the others in this paper. It is that "artiads" have even atomic weights and "perissads" have odd atomic weights, with the single exception of nitrogen. That is, those elements which have even valencies have even atomic weights, and those elements which have odd valencies have odd atomic weights, with the exception of nitrogen.

This observation only applies to elements of less atomic weight than 63, because after this the difference between the two series of atomic weights is greater than 0·5, and it is impossible to decide whether the atomic weight approximates to an even or an odd whole number.

The atomic weights of the twenty-eight elements concerned in this investigation are now given as determined by the International Committee on Atomic Weights (1905). (See Table I.).

TABLE I.

Element.	Symbol.	O=16.	H=1.	Obvious whole number.
Hydrogen ..	H	1·008	1·000	1
Helium ..	He	4	4	4
Lithium ..	Li	7·03	6·98	7
Glucinum ..	Gl (Be)	9·1	9·03	9
Boron	B	11·0	10·9	11
Carbon . ..	C	12·0	11·91	12
Nitrogen ..	N	14·04	13·93	14
Oxygen . ..	O	16·00	15·88	16
Fluorine ..	F	19	18·9	19
Neon	Ne	20	19·9	20
Sodium ..	Na	23·05	22·88	23
Magnesium .	Mg	24·38	24·18	24
Aluminium .	Al	27·1	26·9	27
Silicon . ..	Si	28·4	28·2	28
Phosphorus .	P	31·0	30·77	31
Sulphur ..	S	32·06	31·82	32
Chlorine ..	Cl	35·45	35·18	35
Potassium ..	K	39·15	38·85	39
Argon	A	39·9	39·6	40
Calcium ..	Ca	40·1	39·7	40
Scandium ..	Sc	44·1	43·8	44
Titanium ..	Ti	48·1	47·7	48
Vanadium ..	V	51·2	50·8	51
Chromium ..	Cr	52·1	51·7	52
Manganese .	Mn	55·0	54·6	55
Iron	Fe	55·9	55·5	56
Cobalt . ..	Co	59·0	58·55	59
Nickel	Ni	58·7	58·3	59

3. The third observation is that all the numbers under O = 16 are either equal to whole numbers or *greater than* whole numbers, except A, Fe, and Ni. The property of magnetism in the two latter elements may account for the slight diminution of atomic weight.

(B). The second deduction is that the increase in the atomic weights of elements above whole numbers is due to the condensation of protyle within each atom, and that this condensation accounts for the observed emission under certain conditions of exceedingly small material particles from substances.

4. The fourth observation is that, in nine instances, a difference of 4 in the list of "obvious whole numbers" corresponds to a difference of two valencies. The nine instances are given in Table II.

TABLE II.

Li	Monad ..	7	4	Na	Monad ..	23	4
B	Triad ..	11		Al	Triad ..	27	
Mg	Dyad ..	24	4	Al	Triad ..	27	4
Si	Tetrad ..	28		P	Pentad ..	31	
Si	Tetrad ..	28	4	P	Pentad ..	31	4
S	Hexad ..	32		Cl	Heptad ..	35	
Ca	Dyad ..	40	4	Sc	Tetrad ..	44	4
Sc	Tetrad ..	44		Ti	Hexad ..	48	
V	Pentad ..	51	4				
Mn	Heptad ..	55					

5. The fifth observation is that in every case the above increment of 4 corresponds to an addition of two *acidic* forces; or, in other words, of two forces the nature of which has caused all elements containing them to be classed as non-metallic.

6. The sixth observation is that one of this pair of forces emanates from a portion of the element whose mass is 1, and the other from a portion of the element whose mass is 3. This is evident from Table III.

TABLE III.

B	Triad ..	11	1	Na	Monad ..	23	1
C	Tetrad ..	12		Mg	Dyad ..	24	
Al	Triad ..	27	1	P	Pentad ..	31	1
Si	Tetrad ..	28		S	Hexad ..	32	
K	Monad ..	39	1	V	Pentad ..	51	1
Ca	Dyad ..	40		Cr	Hexad ..	52	
Mg	Dyad ..	24	3	Si	Tetrad ..	28	3
Al	Triad ..	27		P	Pentad ..	31	
S	Hexad ..	32	3	Cr	Hexad ..	52	3
Cl	Heptad ..	35		Mn	Heptad ..	55	

(C). The third deduction is that the acidity or non-metallic nature of an element is always due to a pair or pairs of electro-positive forces, each pair emanating from a portion of the element, of which the mass is 4, taking the mass of an atom of hydrogen as unity.

7. The seventh observation is that acidic forces always occur in pairs.

8. The eighth observation is that, if the values given for the atomic weights of certain elements be reduced in the ratio 35·45 : 35, these reduced values approximate to whole numbers. The elements referred to are Be, Mg, Si, and Cl. The atomic weights of the first three are especially dependent upon that of Cl. Bromine will also be considered in this observation, since its value is well known to be especially dependent upon that of Cl.

The atomic weights of these five elements, when reduced in the ratio 35·45 : 35, become 8·997, 24·05, 28·04, 35, 78·94 respectively.

Before the reduction, bromine's value (79·96) was already nearly a whole number, but that is probably quite accidental—for, being a perissad, its atomic weight should be an odd number.

(D). The fourth deduction is that the weight of an atom of Cl, together with its condensed protyle, has been correctly ascertained to be 35·45; but that, when the atomic weight of another element is being compared with and obtained from that of Cl, the latter should be taken as 35 instead of 35·45.

9. The ninth observation is that the constitution and structure of each element can be deduced in a rational and uniform manner by taking into consideration all the above observations and deductions, and the portion of each element which is metallic is thereby made evident.

The constitution and structure of several elements will now be given, as obtained in accordance with the observations and deductions given above.

THE

APPLICATIONS OF GRIGNARD'S REACTION.*

By ALEX. McKENZIE, M.A., D.Sc., Ph.D.

(Concluded from p. 169).

SECTION II.

Preparation of the Grignard Reagent.

IT is of paramount importance that the materials used in the preparation of the Grignard reagent should be as dry as possible. The following description of the preparation of magnesium methyl iodide is given by Grignard (*Revue Générale des Sciences*, 1903, xiv., 1041). The magnesium (24 grms. 1 atom) is placed in a round-bottomed flask to which are attached a dropping-funnel and a reflux condenser. Methyl iodide (1 mol.) is mixed with an equal volume of anhydrous ether and 25 to 30 cc. of the mixture added to the magnesium. After a few minutes a vigorous action takes place, and at this stage 200 to 250 cc. of anhydrous ether are added; the rest of the mixture of methyl iodide and ether is then gradually added by means of the dropping-funnel. Finally the mixture is warmed if necessary—that is, if the magnesium has not already been all dissolved. Under these conditions one obtains an almost colourless liquid, and there is practically no sediment.

In preparing magnesium methyl iodide in much smaller quantity than indicated by Grignard in the preceding description, the magnesium may be placed in a round-bottomed flask, connected with a condenser, which is provided with a tube, containing calcium chloride and soda lime. The mixture of methyl iodide and about four times its volume of ether is then added in one lot to the magnesium. The action is moderated, if necessary, by immersing the flask in ice-cold water.

The following points regarding the preparation of the reagent may be noted:—

1. *Magnesium.*—Powder, ribbon, or filings are employed by various investigators. The filings, provided by the Aluminium- and Magnesium-Fabrik, Hemelingen, bei Bremen, are very suitable; according to Klages they contain 99·7 to 99·8 per cent of magnesium. Evidence is not wanting to show that impurities in the magnesium sometimes affect the reaction. Beckmann (*Ber.*, 1905, xxxviii., 904) shows that calcium may be substituted in certain cases for magnesium, but the method does not appear to present any advantages over the usual one.

2. *Ether.*—The ether should be thoroughly dried by the following method, for example. Wash with water, dry with calcium chloride, filter, add sodium wire, distil over sodium wire and then over phosphorus pentoxide (compare Perkin and Pickles, *Trans. Chem. Soc.*, 1905, lxxxvii., 647). Ullman and Münzhuber (*Ber.*, 1903, xxxvi., 406) prepare their anhydrous ether by shaking 300 cc. of ordinary ether (sp. gr. 0·722) with a mixture of 25 cc. of concentrated sulphuric acid and 25 cc. of water and then allowing the product to remain for one to two hours over a little sodium wire.

The presence of the merest trace of water is shown up, in the carrying out of a Grignard action, by the slight turbidity which appears when the action starts, and which thereafter disappears.

That the method of drying the ether may have an important influence on the progress of the action is indicated by the experience of Ahrens and Stapler (*Ber.*, 1905, xxxviii., 1296, 3259), In their first communication on the use of dihalogenides those authors showed that ethylene dibromide readily interacts with magnesium and ether to form the compound $MgBr.CH_2.CH_2Br.(C_2H_5)_2O$. Since, however, on repetition of this experiment with the same samples of magnesium and ethylene dibromine the chief product was magnesium bromide, it was obvious that the action

* A Paper read before the British Association (Section B), Leicester Meeting, 1907.

depended on the state of the ether. Experiments showed how varying the results were, according to the manner in which the ether was dried.

It should also be remembered that the ether may contain negative catalysers, which may either retard the action or prevent it. Bischoff points out, for example, that magnesium is not dissolved by a mixture of ethylene dibromide and ether in the presence of a little acetone or acetophenone when the mixture is allowed to remain for a night at the ordinary temperature or when it is boiled (*Ber.*, 1905, xxxviii., 2078). This action of a negative catalyser very likely accounts for the fact that occasionally one investigator finds the preparation of some particular Grignard reagent to proceed with ease, whilst another encounters difficulties.

3. *Halogen Compound.*—This ought also to be as free from moisture as possible. It does no harm to distil before use.

The ease with which the Grignard reagent is made depends on the particular halide used. Sometimes the action begins of its own accord with readiness, as in the case of magnesium methyl iodide. Sometimes the mixture requires to be heated, but when once started the action proceeds to a completion after the source of heat has been withdrawn. In other cases the mixture must be continuously heated. Occasionally a catalyser is necessary to start the action vigorously.

It frequently happens that, in addition to the formation of the Grignard reagent, a secondary reaction takes place, namely, the formation of saturated hydrocarbons by the action of magnesium on the halide, for instance, $2C_6H_5Br + Mg = MgBr_2 + C_6H_5.C_6H_5$ (Tissier and Grignard, *Comptes Rendus*, 1901, cxxxii., 835; Tschelinzeff, *J. Russ. Phys. Chem. Soc.*, 1904, xxxvi., 549; Tiffeneau, *Comptes Rendus*, 1904, cxxxix., 481). Diphenyl is always formed in this manner in the preparation of magnesium phenyl bromide. With alkyl halides with low molecular weight this secondary reaction is not pronounced, but with halides of higher molecular weight it is difficult to work with calculated amounts owing to this reaction taking place to a marked extent. According to Grignard (*Ann. Chim. Phys.*, 1901, xxiv., 450; Houben, *Ber.*, 1903, xxxvi., 2897), magnesium, allyl iodide, and ether give the compound C_3H_5MgI,C_3H_5I, that is, all the metal is not attacked in the action.

4. *Importance of Completing Solution of the Magnesium.*—It is not desirable to use a Grignard reagent containing an excess of the halide; calculated amounts of magnesium and halide should be used and the solution of the magnesium completed so far as possible. It should be noted that action between magnesium alkyl halide and excess of alkyl halide can take place with formation of hydrocarbon, $RMgBr + RBr = MgBr_2 + R.R$ (Houben, *Ber.*, 1903, xxxvi., 3084).

5. *Substitution of other Solvents for Ether.*—It may be at once stated that ether is by far the most convenient solvent.

Brühl shows that bromocamphor, for example, when mixed with benzene or xylene, dissolves magnesium at elevated temperatures (*Ber.*, 1903, xxxvi., 668, 4272; 1904, xxxvii., 746; Malmgren, *Ber.*, 1903, xxxvi., 2608). Anisole (Malmgren, *Ber.*, 1903, xxxvi., 2619; Houben, *Ber.*, 1905, xxxviii., 3019), amyl ether (Hibbert and Sudborough, *Trans. Chem. Soc.*, 1904, lxxxv., 933), and toluene (Bodroux, *Comptes Rendus*, 1904, cxxxviii., 700) have also been substituted for ethyl ether in certain reactions. Tschelinzeff (*Ber.*, 1904, xxxvii., 2081) shows that, in the formation of Grignard's reagent, ether may be replaced by dimethylaniline. The reaction between dimethylaniline (2 mols.), ethyl iodide (1 mol.), and magnesium (1 atom) is assisted by the addition of a trace of iodine, but the magnesium does not dissolve so quickly as when ether is used. The method was used for the preparation of phenyl ethyl carbinol from benzaldehyde and of phenyl methyl ethyl carbinol from acetophenone. That tertiary amines do actually combine with magnesium organic compounds was subsequently shown by F. and L. Sachs (*Ber.*, 1904, xxxvii., 3088), who obtained, for example, the compound C_9H_7N,C_6H_5MgBr by the action of an ethereal solution of magnesium phenyl bromide on quinoline. Tschelinzeff (*Ber.*, 1904, xxxvii., 4534; *Chem. Zeit.*, 1906, xxx., 378), arguing that tertiary amines form compounds of the type RRRN.RX, has accordingly devised the following modification in the preparation of the Grignard reagent, where a tertiary amine acts as a catalyser. Inert solvents, like benzene, toluene, xylene, hexane, light petroleum, and various terpene hydrocarbons may be used in place of ether if a few drops of a tertiary amine are added. In the case of benzene the following procedure is adopted. The mixture of anhydrous benzene, halogen compound magnesium, and a drop or two of dimethylaniline is heated to boiling until the beginning of the reaction is indicated by the appearance of white flakes; the reaction then proceeds without the application of external heat, and is finally completed by heating. The addition of a little iodine facilitates the starting of the action. In spite of the insolubility of the product, which separates as the type R.MgX, it is claimed that the action is much more energetic and often proceeds more quickly than when ether is used. Further, in those cases where the reagent is formed with difficulty by the ordinary method, the higher temperature at which the Tschelinzeff reagent is formed would appear to be an advantage.

The author of this report has tried the Tschelinzeff method, with little success, however. In spite of what is claimed for it, the method, so far at least, has a theoretical interest only: it does not appear to have been applied at all, except in the very few cases mentioned by Tschelinzeff himself.

6. *Acceleration of the Formation of the Reagent.*—Tissier and Grignard (*Comptes Rendus*, 1901, cxxxii., 1182) found that, whilst alkyl bromides or iodides in ethereal solution as a rule readily interact with magnesium, the action with aryl halides is accelerated by heating or by the addition of a trace of iodine. A drop of methyl iodide serves the same purpose (Klages, *Ber.*, 1904), xxxvii., 1449); this may be used, for example, in the preparation of magnesium α-naphthyl bromide. Iodine and methyl iodide are the catalysers generally used. Monochlorides may not interact with magnesium and ether alone, but do so when a trace of iodine is added (Compare Hesse, *Ber.*, 1906, xxxix., 1146). Aluminium chloride and hydriodic acid may also be used as catalysers (Zelinsky, *Journ. Russ. Phys. Chem. Soc.*, 1903, xxxv., 399). An interpretation for the use of iodine in the formation of magnesium organic compounds from chlorides is advanced by Wohl, namely, $2RCl + MgI_2 = 2RI + MgCl_2$, $2RI + 2Mg = 2RMgI$, $2RMgI + 2RCl = 2MgCl + 2RI$ (*Ber.*, 1906, xxxix., 1952).

In cases where interaction with the halide could not be effected by the usual methods, special devices have been employed. Thus, Ehrlich and Sachs (*Ber.*, 1903, xxxvi., 4296) found that an ethereal solution of *p*-bromodimethylaniline is not acted on by magnesium even when the mixture is heated for several days in the presence of a little iodine. The interaction, however, was brought about as follows:—The magnesium is covered with absolute ether and ethyl bromide added; the action soon becomes vigorous, as usual, and is then moderated by cooling the flask in ice-cold water; the supernatant liquid is poured off quickly from the magnesium and an ethereal solution of *p*-bromodimethylaniline is then added. By this treatment the magnesium had been rendered more active, and the magnesium compound desired was readily obtained by gentle warming. The fact, however, that the yield was far from quantitative, and that the product was necessarily mixed with a little magnesium ethyl bromide, occasioned v. Baeyer to try other methods to make the magnesium active (*Ber.*, 1905, xxxviii., 2759). This result is attained when the magnesium is coated with a thin layer of its iodide. Magnesium filings were heated in a round-bottomed flask over a free flame with constant shaking and half the weight of iodide gradually added. The tem-

perature must not be so high as to cause the mass to melt. With 10 grms. of magnesium this operation requires from fifteen to thirty minutes. The product obtained must be protected carefully from moisture. This "activirtes" magnesium was used by Baeyer himself for the preparation of the magnesium compounds of the iodoanilines and iododimethylanilines, and good results were also obtained by Gomberg and Cone (*Ber.*, 1906, xxxix.. 1467), with diphenylbromomethane when other methods failed.

Kay and Perkin find that commercial magnesium powder sometimes does not interact with *iso*propyl iodide in ethereal solution (*Trans. Chem. Soc.*, 1905, lxxxvii., 1081). When, however, the magnesium is left in contact with an ethereal solution of methyl iodide until the action is vigorous, then washed thoroughly with ether, and at once mixed with the ethereal solution of *iso*propyl iodide, the action proceeds satisfactorily.

7. *Importance of Preventing Oxidation of the Reagent.*—It should be noted that Bouveault and Bodroux have found that the Grignard reagent is acted on by oxygen to form primary alcohols or phenols, so that not only should the reagent be protected from moisture and carbon dioxide, but it should not be left unnecessarily long in contact with air before being applied. Sometimes, indeed, it is necessary to prepare the reagent in an atmosphere of hydrogen (Tschitschibabin, *Ber.*, 1905, xxxviii., 561; Tschelinzeff, *Ber.*, 1906, xxxix., 774).

Methods of Applying the Grignard Reagent.

As a general rule, the compound to be acted on is dissolved in anhydrous ether and the solution either added to the Grignard reagent or *vice versâ*. It is convenient to perform this operation by means of a syphon, and to take precautions that moisture and carbon dioxide are excluded. As a rule, the action requires to be regulated, otherwise it may become too violent. When the addition is complete, sometimes the mixture is heated. Powdered ice is then gradually added, then mineral acid. The product of the action is generally in the ethereal solution.

The following description, taken at random, is typical. It is the method used by Ullmann and Münzhuber for the preparation of triphenylcarbinol from methyl benzoate (*Ber.*, 1903, xxxvi., 406).

A mixture of magnesium (7·2 grms), freshly distilled bromobenzene (57·2 grms., 2·5 mols.), anhydrous ether (60 to 70 grms.), and a trace of iodine is placed in a large round-bottomed flask provided with a reflux condenser and then gently warmed. As soon as the brownish liquid is decolorised and is boiling rapidly it is cooled by immersing the flask in ice-cold water; the action is regulated so that the boiling continues to be vigorous. After twenty minutes the bulk of the magnesium is dissolved; it is practically all gone after the boiling has been continued for half-an-hour longer. The flask containing the reagent is then placed in ice-cold water, and by means of a dropping-funnel a solution of 20 grms. of methyl benzoate (freshly distilled) in an equal volume of anhydrous ether gradually added. The action is vigorous. After the addition of the ester the mixture is heated to boiling for about an hour, ice-cold water gradually added, and then dilute sulphuric acid. The ether is expelled from the ethereal solution, and the product distilled in steam to remove unchanged bromobenzene and a small amount of diphenyl; the triphenylcarbinol remains in the flask. Yield of crude product, 33 grms. (87 per cent); when crystallised from alcohol 28 grms. of pure product are obtained.

Of course this method of working cannot always be adopted. Water in some cases must not be added to the product of the action (compare Kipping's work on silicon compounds). Again, in the action of carbon dioxide and other gases on the Grignard reagent special methods have to be used. Occasionally the temperature at which the reaction is conducted is maintained below 0° (Kohler and Heritage, *Am. Chem. Journ.*, 1905, xxxiii., 21). Sometimes ammonium chloride solution is used in place of mineral acid after the addition of ice (Tilden and Stokes, *Trans. Chem. Soc.*, 1905, lxxxvii., 837); thus in the preparation of phenylmethyltriazene by the action of magnesium methyl iodide the action of acid must be avoided, otherwise the very labile diazoamino-compound undergoes decomposition (Dimroth, *Ber.*, 1903, xxxvi., 909; 1905, xxxviii., 670; compare also Klages, *Ber.*, 1905, xxxviii., 2219).

A perusal of the literature shows that it is often by no means immaterial whether the Grignard reagent is added to the compound to be acted on, or *vice versâ*. This is especially true when one deals with a compound presenting several points of attack for the Grignard reagent. This aspect does not appear to have been fully recognised by a considerable number of investigators in this field. Further, the heating of the product obtained after mixing the Grignard reagent and substance acted on often has an important bearing on the result.

SECTION III.

Theoretical.

The formation of Grignard's reagent was first represented by an equation such as $CH_3I + Mg = CH_3MgI$ (Grignard, *Comptes Rendus*, 1901, cxxxii., 558), and it is convenient to interpret the various reactions as being due to the type R.MgX. The fact, however, that the reaction takes place with such ease in the presence of absolute ether suggested to Grignard himself ("Thèses sur les Combinaisons Organomagnésiennes Mixtes et leurs Applications à des Synthèses," Lyon, 1901) and to Blaise (*Comptes Rendus*, 1901, cxxxii., 839) that the ether is not simply a solvent in the ordinary sense, but is one of the necessary materials for the action. If the reaction product obtained from magnesium, ethyl iodide, and ether is heated under diminished pressure in a current of hydrogen, the residue contains the compound $C_2H_5MgI,(C_2H_5)_2O$, in which the ether is so firmly bound that it is only partially eliminated when the compound is heated under diminished pressure at 100—125°. The compound $C_2H_5MgBr,(C_2H_5)_2O$ exhibits a similar stability towards heat.

Whereas Grignard and Blaise at the time regarded the ether in these compounds as playing the rôle of ether of crystallisation, Baeyer and Villiger (*Ber.*, 1902, xxxv., 1201) formulate the compounds in question on the basis of the quadrivalency of oxygen, thus: $\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!>\!O\!<\!\begin{matrix}MgR\\X\end{matrix}$. Where R represents the alkyl or aryl group, and X the halogen atom. The existence of oxonium compounds, such as $\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!>\!O\!<\!\begin{matrix}SnCl_3\\Cl\end{matrix}$ and $\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!>\!O\!<\!\begin{matrix}C(C_6H_5)_3\\C(C_6H_5)_3\end{matrix}$ (Gomberg), is adduced in support of this view. Again, Ahrens and Stapler (*Ber.*, 1905, xxxviii., 3259) formulate the compound obtained from ethylene dibromide thus:—

$$\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!>\!O\!<\!\begin{matrix}Br\\Mg.CH_2.CH_2Br\end{matrix}$$

The theoretical aspect of the Grignard reaction has been pecially studied by Tschelinzeff. In an early paper he concludes that the ether in the preparation of the Grignard reagent in the usual manner plays the part of a catalyser (*Ber.*, 1904, xxxvii., 4534). He found that interaction between magnesium and alkyl halides took place in benzene solution only when the mixture was heated strongly. In the presence of a little ether (or of anisole), however, the reaction took place at a much lower temperature, at which no action occurred when the ether (or anisole) was absent; the action was very slow, requiring from one to two days for its completion. The white mass which separated contained no ether, exhibited all the ordinary reactions of magnesium organic compounds, and was formed in considerable yield. The point is that this effect was produced by means of a small amount of ether.

Reference has already been made in Section II. to Tschelinzeff's use of tertiary amines as catalytic agents. In a subsequent communication (*Ber.*, 1905, xxxviii., 3664), Tschelinzeff describes thermo-chemical experiments in

which the heat evolved by the action of ether on the ether-free compounds obtained by this catalytic method was measured:—

$$RMgI + \begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!>\!O = \begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!>\!O\!<\!\begin{matrix}MgR\\I\end{matrix} + T.$$

The formula of Baeyer and Villiger is preferred to $\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!>\!O\!<\!\begin{matrix}MgX\\R\end{matrix}$ (Grignard), or to the representation from Werner's standpoint, $\left(\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!>\!O \ldots MgR\right)X$ (*Annalen*, 1902, cccxxii., 261; the theory of the Grignard reagent is also discussed by Abegg, *Ber.*, 1905, xxxviii., 4112). Although ether is not readily eliminated from the complex $\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!>\!O\!<\!\begin{matrix}MgR\\X\end{matrix}$, it is possible to study the heat effect produced by the change—

$$(C_2H_5)_2O + RMgX = \begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!>\!O\!<\!\begin{matrix}MgR\\X\end{matrix},$$

since it is possible to prepare the "individual" magnesium compounds free from ether. Tschelinzeff concludes that in the preparation of the Grignard reagent by the ordinary method there are two distinct reactions:—(1) The formation of the magnesium alkyl (or aryl) halide, and (2) the transformation of this into an ether complex.

Tschelinzeff (*Ber.*, 1906, xxxix., 773) next points out that, after all, those ether complexes were characterised by Grignard and Blaise subsequently to heating the Grignard reagent under diminished pressure. It is not justifiable to assume, as is generally done, that those same complexes actually exist under the conditions which obtain when the Grignard reagent is made in the usual manner. Tschelinzeff, in his previous paper (*loc. cit.*), although actually showing that at least one ether complex is formed, does not prove that the formation of additional complexes is impossible. Now Zelinsky (*Journ. Russ. Phys. Chem. Soc.*, 1903, xxxv., 399) has obtained the compound $MgI_2,2(C_2H_5)_2O$, and Tschelinzeff the compound $MgI_2,4(C_2H_5)_2O$. The analogy is accordingly drawn between the formulæ $(C_2H_5)_2OI.Mg.I(C_2H_5)_2O$ and $R.Mg.I(C_2H_5)_2O$.

Now, since the magnesium iodide complex, $[(C_2H_5)_2O]_2I.Mg.I[(C_2H_5)_2O]_2$, is known, the question naturally suggested itself as to the possibility of analogous ether complexes of the type $R.Mg.I[(C_2H_5)_2O]_2$. The compounds $C_3H_7MgI,2(C_2H_5)_2O$ and $C_5H_{11}MgI,2(C_2H_5)_2O$ were accordingly isolated.

These results, based on analytical and thermo-chemical experiments, prove conclusively, according to Tschelinzeff, that in the preparation of magnesium organic compounds by Grignard's method one obtains ether complexes with two molecules of ether, for which the formulation $\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!>\!O\!<\!\begin{matrix}MgR\\I:O\end{matrix}\!<\!\begin{matrix}C_2H_5\\C_2H_5\end{matrix}$ is suggested (compare also Tschelinzeff, *Ber.*, 1906, xxxix., 1674, 1682, 1686).

Tschelinzeff (*Ber.*, 1907, xl., 1487) also shows that the "individual" magnesium organic compounds are also capable of forming complexes with tertiary amines, thus: $RRRN\!<\!\begin{matrix}MgR\\I\end{matrix}$. These aminates are analogous to monoetherates. No complexes have yet been described analogous to dietherates.

The question of the constitution of the oxonium compounds formed in the preparation of the Grignard reagent by the ordinary method is still, however, under discussion. Tschelinzeff (*Comptes Rendus*, 1907, cxliv., 90) points out that if Baeyer's formulation, $\begin{matrix}R\\R\end{matrix}\!>\!O\!<\!\begin{matrix}MgR'\\X\end{matrix}$, is accepted, two isomerides are possible, namely, $\begin{matrix}R\\R\end{matrix}\!>\!O\!<\!\begin{matrix}MgR'\\X\end{matrix}$ and $\begin{matrix}R\\R'\end{matrix}\!>\!O\!<\!\begin{matrix}MgR\\X\end{matrix}$; whereas if Grignard's formulation, $\begin{matrix}R\\R\end{matrix}\!>\!O\!<\!\begin{matrix}MgX\\R'\end{matrix}$, is correct no isomerism is possible. Tschelinzeff claims to have established the existence of isomerides. Grignard, however (*Bull. Soc. Chim.*, 1907, [4], i., 255), maintains that his formula permits of the conception of isomerides, and regards it as more plausible than Baeyer's.

THE QUANTITATIVE SYNTHESIS OF ARGENTIC NITRATE, AND THE ATOMIC WEIGHTS OF NITROGEN AND SILVER.*

By THEODORE WILLIAM RICHARDS
and
GEORGE SHANNON FORBES.

Introduction.

THE composition of argentic nitrate is one of the questionable premises in the lively argument which has recently taken place concerning the atomic weights of nitrogen and silver. (See especially Guye, "Nouvelle Rech. s. l. Poids Atom. de l'azote," Soc. Ch., Paris, 1905. The reader is referred for a convenient *résumé* to the "Report of the International Committee on Atomic Weights," *Journ. Am. Chem. Soc.*, 1906, xxviii., 1, and many other places; also to Clarke, *Journ. Am. Chem. Soc.*, 1906, xxviii., 293; Gray, *Trans. Chem. Soc.*, 1906, lxxxix., 1173). Although Stas's syntheses of this salt were carried out on a large scale, and far more carefully than those of anyone before him, several points concerning the details of the work were not investigated with the care which modern physico-chemical knowledge demands. Accordingly, a repetition of this work of Stas's seemed to be worth the trouble involved, and the following pages contain a brief account of nine months' thought and labour upon it.

The method appears at first sight to be extremely simple, consisting merely in the weighing of pure silver, the dissolving of this silver in nitric acid, and the weighing of the resulting nitrate. The preparation of pure silver having been already solved, the great difficulty consisted in the procuring of satisfactory evidence that the nitrate was free from impurity, and in making sure that none of the silver was lost during the process. The main emphasis of the subsequent discussion will therefore be laid on these points, the other details being often indicated with but few words, because they so closely resemble the details of previous investigations carried out in the Chemical Laboratory of Harvard College.

The research naturally divided itself into four sections, namely, first, the preparation of pure materials; second, the quantitative synthesis; third, the determination of the purity of the product; and fourth, the final result and its relations to the table of atomic weights. These will be considered in order.

Preparation of Pure Materials.

All the substances used in the research were purified with very great care. Nitric acid and silver were the two most important.

Nitric acid was supplied by two firms. Each sample was warranted by the manufacturers to be of a very high grade of purity. Each was re-distilled twice just before adding to the silver, using only the middle portion of each distillate. None of the samples left a trace of non-volatile residue on evaporation. No difference could be detected in the results because of the difference of source of the acid, nor was the constancy destroyed when a single distillation only was made (Experiment 11). Hence little anxiety was felt concerning the purity of this material.

Silver.—The researches of Richards and Wells have shown how to prepare silver of unquestioned purity. Preliminary determinations 1, 2, 3, 4, 5, 7, and 8 were made on a sample (A) left over from the above-mentioned research, crystallised fifteen times with nitric acid, precipitated with formate, and fused on purest charcoal, but

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not electrolysed or fused in hydrogen. No. 9 was made with a sample prepared by Prof. Baxter for his final work on bromine. It had been through the chloride and formate treatment, electrolysed, fused in hydrogen, cut with a saw, etched with nitric acid, boiled with water, dried at dull redness *in vacuo*, and given us ready to weigh. We are much indebted to him for furnishing this check on our silver. The final determinations were made with silver derived from several preparations. The first of these (C) was re-crystallised sixteen times as nitrate from water and re-distilled nitric acid, and then precipitated twice in succession with formate. A part of the final formate product was fused on the best lime in carefully purified hydrogen made from aluminium and sodic hydroxide. Sample D had been precipitated as chloride, reduced with best alkaline sugar, washed free from chloride, dissolved in nitric acid, filtered, and crystallised as nitrate in platinum six times from nitric acid distilled in a platinum condenser. Centrifugal treatment eliminated the mother-liquor. The last crop of crystals was precipitated with formate in a silver dish, washed free from ammonia, and fused in a cup of pure lime. Sample F was obtained by the electrolysis of a button of very pure silver from Colorado, which had been fifteen times re-crystallised as nitrate, precipitated with formate, and fused on lime. Samples C, D, and F were all cleaned by etching, and then purified by electrolysis through a nitrate solution made from some of the same silver and the purest nitric acid. They were then fused separately, on a well-seasoned lime boat, in a new porcelain tube, in an atmosphere of pure electrolytic hydrogen. The Hempel stoppers fitted so well that the pressure could easily be reduced to a fraction of a millimetre by a Geryk oil-pump when desired. The heating was accomplished by a large Heraeus electric furnace which fused the silver without overheating any part of the tube. In all cases the initial fusion was completed in hydrogen at atmospheric pressure, but in half the fusions the tube was evacuated before the temperature was lowered. No spirting or boiling could be observed through the glass window when the pressure was reduced, and the silver thus prepared gave the same combining weight as that cooled under a full atmosphere's pressure of hydrogen. Thus the conclusion of Richards and Wells, and of Baxter, that silver cannot dissolve a weighable amount of hydrogen, was confirmed.

The buttons thus obtained were etched to remove lime, and if too large to go into the flasks used for the synthesis, were cut with a cold chisel or a jeweller's saw, observing all the precautions recommended by Richards and Wells. The fragments freed from superficial iron were washed and dried, sometimes in the electric oven in air at 150° for an hour, sometimes in a vacuum at dull redness, and sometimes in a reduced pressure of hydrogen. Judging from the constant combining weight, all these methods were equally good.

Water.—The water was distilled first with alkaline permanganate through a glass condenser, and then, after the addition of a small drop of dilute sulphuric acid, through a carefully cleaned condenser of block tin. Needless to say, dust was excluded as much as possible, and distillations were conducted immediately before the water was needed, in order to avoid absorption of gases or solution of solid matter.

Air.—It will be remembered that Stas allowed his solutions of argentic nitrate to evaporate very slowly, the vapours diffusing out through the neck of his flask, and condensing in a suitable receptacle. Under these conditions the evaporation required seventy-two hours of continuous heating—an unnecessarily prolix process. To hasten the escape of aqueous vapour, it was resolved to maintain a gentle current of pure dry air throughout the process. The air for this purpose was delivered from a water-pump, which must have removed some of the original impurities. It was passed first through a tall Emmerling tower filled with beads moistened with concentrated sulphuric acid, to which a trace of potassic bichromate had been added, and then through two more towers filled with a concentrated solution of pure potash, being thus freed from ammonia and from acid gases. Next it was passed through a tall drying tower of stick potash, to a hard glass tube containing platinised asbestos heated to dull redness by a Bunsen burner. The hot platinum was intended to destroy organic matter. Hence it passed into a trap designed to catch asbestos shreds, and finally, the air was dried by two towers of broken potash. The whole purifying train was put together without rubber, all the pieces being blown together except the hard glass tube, which was connected with the soft glass on either side with joints so well ground that no lubricant was necessary. The towers were glass-stoppered. Air thus purified and dried contains nothing to injure the silver nitrate except possibly a minute trace of ammonia, which might have come out of the potash solutions.

The Synthesis of Argentic Nitrate.

The materials having been prepared, the next step was to combine them. This combination must take place in a vessel wholly free from a suspicion of solubility on the one hand, and arranged so as to prevent loss of material on the other hand. At the same time, it was important to be able to evaporate and to weigh the argentic nitrate in the same vessel. After a careful consideration of the somewhat conflicting claims of these requirements, it was decided to carry out the process in small round-bottomed flasks of fused quartz of from 0·03 to 0·04 litre capacity; with necks 11 cm. in length and 6 to 9 mm. in internal diameter. Collars of platinum-wire provided with loops permitted the suspension of these flasks from the hook of the Troemner balance. Before weighing, they were heated in the oven, to be presently described, to 250° for at least half an hour, a moderate air-current sweeping through them all the time. The coverings were then lifted, and each flask was removed by a hook of platinum-wire sealed into a glass rod, and transferred to a large desiccator provided with a suitable support. Two flasks similar in weight and surface were treated in the same way, and kept in the same desiccator. After two hours near the balance the first flask was weighed against a tare, its weight being determined by substitution of the first by the second flask and a few small weights. Upon removal from the desiccator both flasks absorbed moisture from the air, often to the extent of 0·0001 grm., but they soon reached constancy with respect to one another, which was all that was needed. No final weighings were made when the hygrometer in the weighing-room stood above 40, and under these circumstances flasks could be weighed on successive days with variations not exceeding 0·00003 grm.

A new Troemner balance, sensitive to 0·01 mgrm., was available for the research. The brass weights were carefully standardised at the beginning at the year, and again upon starting the final series; and the rider also was calibrated, and the necessary correction employed. For correction to the vacuum standard 0·000132 was added to each apparent grm. of argentic nitrate, and 0·000030 was subtracted from each apparent grm. of silver. This was on the assumption that the two specific gravities concerned were respectively 4·35 and 10·49, that of the brass weights being 8·3.

The silver was now weighed by substitution, and carefully pushed down the neck of the flask, which was held meanwhile in a horizontal position to avoid breakage. Next the whole was transferred to a large clean empty desiccator, whose sides had been moistened, and the flask was laid on a suitable support of glass and platinum tilted 45° from the vertical. A sufficient quantity of purest nitric acid mixed with half its volume of distilled water was poured in from the platinum crucible into which it had just been distilled. The cover of the desiccator was replaced, but its stopper was first removed, and covered with a watchglass and a clean beaker. The apparatus was now kept all night in a warm place, between 40° and 50° C.; thus the silver when dissolved remained in solution, though the volume was restricted to 2 cm. of solution per grm. of

nitrate. In the morning the process was found to be complete. After washing down the neck with a few drops of freshly distilled water, the flask was placed in the oven as before. The desiccator was washed with a little water, the washings being tested for silver in the nephelometer; if any had been found it might have been feared that more had escaped, but as no trace was ever found, it was inferred that the long inclined neck had caught all the spray.

Attention is now called to the apparatus for evaporation. (In passing it might be noted that one of us used a somewhat similar arrangement for evaporating solutions of sodic sulphate fifteen years ago, *Proc. Amer. Acad.*, 1891, xxvi., 258). The main feature of this was the combined delivery tube for the air current and hood for the protection of the contents of the flask. This hood, H, with its ingress and egress tubes, I and E, is shown in the diagram (Fig. 1).

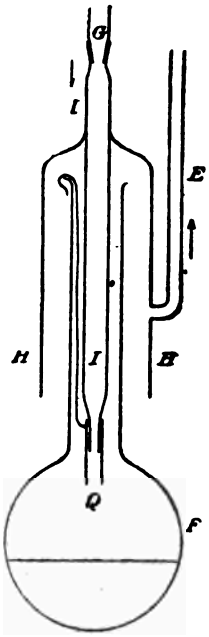

FIG. 1.—APPARATUS FOR EVAPORATING AQUEOUS SOLUTIONS. (Section about half actual size).

F, flask of fused quartz; H, H, protecting hood, with tube, I, for air supply; Q, quartz tube suspended by platinum wire, serving as air nozzle.

The dry air used to sweep out the aqueous and nitrous vapours entered from the purifying train at G, where connection was made by a well-ground joint; passing through the tube I, it escaped into the body of the flask and out through its neck. A side tube, E, was attached to H for connection with a water-pump. The flask rested on a triangle of platinum-wire attached to a glass tripod, and the whole was placed in a 1·5-litre beaker which served as the oven. A sand-bath enabled this to be kept at any desired temperature. The cover of the beaker was of sheet copper, pierced with three holes, for the tubes I and E, and for the thermometer. As no nitrous fumes escaped into the oven, this cover remained intact. In the preliminary trials the extra tube Q was lacking, the tube I being extended to take its place. The part which had projected into the body of the flask was treated with hot dilute nitric acid, and investigated for silver in the nephelometer. Occasionally some was found, but the corrections required were not large. Nevertheless, the possibility that the fused nitrate had attacked the glass was always disturbing, and the inconvenience and uncertainty of this correction made its elimination desirable. Accordingly, in the final determinations, a section of quartz tubing, Q, 3 mm. in diameter and 15 mm. long, was firmly attached to a platinum-wire and lowered till it barely projected into the body of the flask. This supporting wire hooked into the collar, so that the quartz tube could be removed while the silver was dissolving. During the evaporation, however, it was in place, and the end of the glass delivery tube was shortened and drawn down to fit into it. The glass tube was still tested as before, but no silver was ever recovered from it. Hence the flask and the quartz tube must have retained all the silver originally weighed out.

The evaporation of the liquid was easily and quickly conducted in this apparatus. If the flask was not more than half full, and the air passed through the drying train no faster than two bubbles per second, it was possible to maintain the temperature of the oven at 125° without risk of ebullition. The vapours drawn out as before described passed first through a U-tube filled with moist glass beads and just sealed with water, afterwards through a tower of caustic alkali to take out nitric acid which might attack the water-pump. When the liquid became coated with a film of crystals the temperature was lowered to 110°; bubbles of vapour now formed gradually under the crystal layer, and the slight spattering caused by their rupture could be seen on the inside walls of the flask. The oven was now suddenly cooled, so that the vapours from the hot liquid, condensing on the walls of the flask, washed down the crust which had formed during evaporation. Upon continuing the heating, a porous crust was soon formed, under which the formation of steam caused no spattering. Finally, the temperature was raised gradually, while the last trace of liquid was disappearing. The solid was dried for a quarter of an hour at 150° in the dark, and then heated to 230° to insure complete fusion, not only of the main portion, but also of any portions projected on the upper walls of the flask. (This temperature, 230°, and the others to be recorded later have not been corrected for the exposed steam; they do not indicate the exact melting-point of the salt). The temperature was soon lowered to 210°, which sufficed to keep the mass in fusion, and the air current was continued for an hour. Then, in subdued light, the flask was lifted out by a loop of platinum-wire passed through its collar, placed on a network of platinum-wire, and tilted in all directions to cause the nitrate to solidify in a thin layer on the walls. Once this precaution was neglected, and the flask was cracked by the contraction of the nitrate on cooling. When the nitrate was wholly solid but still hot, the flask with its contents was transferred to its support of platinum wire in a large tight desiccator, which was wrapped in a black cloth and left near the balance over-night. Then the weight of the flask was determined as before. Thus in the entire cycle of operations nothing but platinum, clean glass, and pure air touched the outside of the flask.

It remains to be proved that no silver was carried out by the air current. This was inferred because no trace of silver was ever found in the U-tube through which all the vapours passed; but more definite evidence was obtained by re-dissolving two finished determinations, and evaporating them again with the customary precautions.

Determination No.	$AgNO_3$ once evaporated.	$AgNO_3$ twice evaporated.	$AgNO_3$ thrice evaporated.	Total gain.
8.	10·68933	10·68928	10·68920	−0·00013
15.	14·20114	14·20122	14·20127	+0·00013
		Average gain or loss		0·00000

The first residue in the case of No. 15 was slightly darkened by prolonged heating; still no fixed tendency toward either loss or gain is shown by these figures, and the reliability of the method is demonstrated.

Two preliminary experiments were not finished, and one was rejected because of known error. Six preliminary determinations carried out in the way just described gave results varying from 157·483 to 157·475 parts of nitrate

from 100·000 parts of silver, in the mean 157·479. This is very nearly the same as the final series, given later, but because of sundry irregularities these determinations are individually much less trustworthy than the latter. One of the preliminary determinations was made with a piece of silver kindly given us by Prof. Baxter for the sake of comparison, and for which we are much indebted. It gave a result perhaps higher than the average, but not by an amount greater than the limit of error of the experimentation at that time. It is greatly to be regretted that this piece was not examined after every detail of the process had been perfected, because the comparison would have been interesting, although not at all essential for the completeness of our work.

When it appeared impossible to improve upon the details of the experimentation, a final series of six consecutive determinations was carried out with all possible care. In each case, except Nos. 14 and 15, the argentic nitrate was maintained for an hour in a fused condition while dry air swept over it. In No. 14 only one-quarter of an hour was allowed, whereas in No. 15 the fusion was prolonged for three hours. Sample D of silver was used in Syntheses 10, 11, and 12, and Sample F in the other three.

The Synthesis of Argentic Nitrate.

No. of synthesis.	Weight of fused silver (in vacuum). Grms.	Weight of fused argentic nitrate (in vacuum). Grms.	Weight of argentic nitrate made from 100·000 parts of silver.
10.	6·14837	9·68249	157·481
11.	4·60825	7·25706	157·480
12.	4·97925	7·84131	157·480
13.	9·07101	14·28503	157·480
14.	9·13702	14·38903	157·481
15.	9·01782	14·20123	157·480
	Average		157·480 (*a*)

(*a*) The probable error of this average, computed from the results when carried to the next decimal place, is only 0·0001, a wholly negligible quantity. Hence repetition of the process was unnecessary.

For this ratio just found to be 100·000 : 157·480, Stas obtained an average of 100·000 : 157·475 from nine determinations, which ranged from 157·463 to 157·488.

Better agreement then that exhibited by the above table could hardly be desired or expected, as the greatest deviation corresponded to less than 0·1 mgrm. in the weight of the argentic nitrate. This series demonstrated that it is not necessary to use very large amounts of material in order to attain a very high order of precision, if only the details of experimentation are fittingly arranged.

Satisfactory as this series of results appears to be, it is by no means to be accepted without further question as representing the true weight of argentic nitrate to be obtained from pure silver. Even in this fused salt, prepared under such favourable conditions, several impurities might exist; and because in each case the method of treatment was the same, these impurities might be constant in amount, and therefore not perceivable in the results. Accordingly, attention was now directed to the search for these impurities, and this part of the investigation was found to be the most arduous and time-consuming part of it. The following section discusses this matter.

(To be continued).

Disecondary Butylene Monochlorhydrine.—Louis Henry. — Disecondary butylene monochlorhydrine, $H_3C—\underset{Cl}{CH}—\underset{OH}{CH}—CH_3$, results from the action of hypochlorous acid, (HO)Cl, upon symmetric dimethyl ethylene, $H_3C—CH=CH—CH_3$. It is a colourless liquid slightly soluble in water; it boils at 138—139° under 753 mm. pressure, and its vapour-density is found to be 3·73 (calculated value, 3·75). It is readily transformed by alkalis and by salts with an alkaline reaction, such as K_2CO_3, into its oxide, $H_3C—\underset{\diagdown O \diagup}{CH—CH}—CH_3$.—*C. R.*, cxlv., No. 11.

ON THE DIRECT QUANTITATIVE SEPARATION OF CHLORIDES AND BROMIDES.

By LAUNCELOT W. ANDREWS.

Introduction.

THE direct separation of chlorine from bromine has always been considered one of the most difficult problems of quantitative analysis, excepting those relating to the rare earths and the radio-active elements. The standard works on quantitative analysis usually content themselves with a discussion of indirect methods, omitting any description of processes for direct separation.

Practically all the methods recommended for the direct separation of these elements rest on oxidation reactions applied to solutions of bromides and chlorides. The difference between the oxidation-potential of a solution of chlorine in potassium chloride and water and that of a corresponding solution of bromine is about 0·241 volt (Bancroft, *Zeit. Phys. Chem.*, 1892, x., 405). Numerous oxidising agents have been employed, always in acid solution, that is in the presence of solutions more or less concentrated as regards hydrogen ions. In every case investigated excepting one the oxidant used possesses a higher oxidising potential than that of an aqueous solution of chlorine. Hence in such cases, the success of the operation must depend on interrupting the process exactly at the point when all bromine is liberated, since if prolonged beyond that point some chlorine would also be set free. Methods subject to conditions of this sort cannot be looked upon as other than empirical. They can give results approximating the truth, only by a minute regard to all the circumstances of the reaction, as temperature, degree of acidity, concentration, &c., and only then by a happy compensation of errors.

Bugarszky (*Zeit. Anorg. Chem.*, 1895, x., 387) first pointed out the necessity of selecting as an oxidant, one of which the oxidising potential should be intermediate between that of chlorine and that of bromine. With this principle in view, he made use of iodic acid as an oxidising agent. It has an oxidation potential 0·064 volt higher, according to Bancroft, than that of an equivalent and equally acidified bromine solution. A very careful examination of Bugarszky's method, in comparison with a considerable number of other methods, has confirmed that investigator's observations in most essential respects, and has convinced me that his is by far the best method yet published. It is true that the process of Engel (*Comptes Rendus*, 1894, cxviii., 1263) is capable of giving reasonably exact results, especially with certain modifications, of which the most important is the exclusion of ammonium salts. The feature of the latter method is the use of a perdisulphate as oxidant. Engel employed the ammonium salt, $(NH_4)_2S_2O_8$. The method has serious drawbacks. One of these is the oxidation of part of the bromide and chloride to bromate and chlorate, which takes place under conditions not easily defined but seemingly due to small amounts of catalysing agents. Since the chlorate and bromate must be afterward reduced and the whole process repeated in order to complete the desired separation, I felt compelled to abandon the method after a good deal of experience with it.

Briefly stated, Bugarszky's method consists in adding to the bromide-chloride solution, sulphuric acid and potassium di-iodate, then distilling. The bromine and iodine liberated in accordance with the equation $KH(IO_3)_2+10KBr+11H_2SO_4 = 11K_2SO_4+10Br+2I+6H_2O$ passed off with the steam. The remaining solution contains the hydrochloric acid and the excess of iodic acid. Bugarszky observed that when the bromine was determined by absorption of the vapour in potassium iodide and subsequent titration of the iodine, the amount of bromine found was considerably less than that taken, in consequence of a portion having been reduced by the steam to hydrobromic acid with liberation of oxygen. He therefore re-

commends determining the bromine by titration of the unconsumed excess of iodate remaining in the mother-liquor. He overlooks, strangely enough, the fact that if the first named procedure gives too low figures for the bromine, the second must lead to results that are too high, because a part of the bromine being reduced to hydrobromic acid in the solution and in the condensed and returned steam, it must be again oxidised at the cost of the iodic acid. This obvious reasoning is fully confirmed by my experiments, which showed always results too high by titration of the iodate excess (by 1·0 to 1·5 per cent). Hence the determination of the bromine should be made by the alternative method of Bugarszky, viz., absorption of the vapour, containing steam, bromine, and hydrobromic acid, in a reducing solution, with following titration of the bromide according to Mohr or Volhard, or gravimetric estimation.

As regards the determination of the chloride in the mother-liquors, I was able to get results of the same accuracy as the test analyses of Bugarszky. These results are satisfactory when the relative amount of chlorine is large, but were not sufficiently so for my purpose when the chlorine percentage is low. The causes of inaccuracy in this case do not lie in any imperfection of the main reaction, but are as follows:—

1. The maximum amount of substance taken by Bugarszky is 0·400 grm. This cannot well be exceeded without other modifications of the method.

2. The presence of considerable quantities of sulphuric acid and sulphates interferes noticeably with the precision of the Volhard method when the amount of chloride is very small, because appreciable amounts of difficultly soluble silver sulphate are dragged down with the chloride and sulphocyanate.

3. Bugarszky gets rid of the iodic acid before determining the chlorine by first reducing to iodide with sulphurous acid, then expelling the iodine by boiling with sodium nitrite. This procedure is open to objection. It is no easy matter to prepare or to buy sodium nitrite free from chloride. (It is to be remembered that silver chloride is to a considerable extent soluble in solutions of sodium nitrite, hence the salt must be wholly decomposed before testing for chloride). If any trace of nitrous acid is left in the solution it will, as is well known, interfere with the sharpness of the end reaction in the Volhard titration. Further, the process leaves a considerable additional amount of foreign salts in solution, and especially of sulphate, disadvantageous for seasons stated under 2. As a matter of fact, it is not necessary to remove the excess of iodic acid at all. If the solution is sufficiently diluted and acidified with nitric acid, iodic acid only interferes in a minor degree with the titration, the error being of about the same order as that introduced by the presence of sulphates; negligible therefore except when the amount of chloride is small.

To increase the accuracy of the method it accordingly seemed advisable, to increase the amount of substance taken, to replace the sulphuric acid by nitric acid, to remove the excess of iodic acid by a single reagent which would introduce no sulphate or other injurious compound, and the excess of which would require no removal. It would take too much space to recount the steps by which these objects were attained, and several additional advantages incidentally gained. Before presenting details of the procedure finally adopted it will suffice to say that the removal of the iodic acid is best effected by the use of phosphorous acid. This substance possesses almost ideal properties for the purpose. Under the conditions, it reduces iodic acid to free iodine, quantitatively, not leaving even the slightest traces of iodide in the solution. The iodine can be readily boiled off, and the excess of phosphorous acid does not in the least interfere with any subsequent operations. Experience has demonstrated that in expelling the bromine it is not sufficient to distil till the solution is colourless as prescribed by Bugarszky, since at this point traces of bromine may still remain as shown by fluorescein paper (Baubigny), or by the still more sensitive tests mentioned below. It proved to be desirable to use an amount of bromide for the analysis, increasing as the amount of chloride diminishes, and an amount of iodate such that the excess of iodic acid shall be approximately constant. A similar consideration is valid for the nitric acid. The effect of this adjustment is, that when the amount of bromine to be expelled is larger the solution is more acid at the beginning, but the final acidity at the close of the reaction is approximately the same. Hence, it does not take much longer to expel the larger amounts of bromine than the smaller, the reaction being slow only when nearly complete.

For the determination of chloride in crude potassium bromide, the following table will serve as a guide to the amounts of substance and reagent to take. In case of other bromides quantities equivalent to those given should be used.

If the KBr—KCl has per cent of KCl.	Weight of KBr+KCl.	Fifth normal iodate, KIO_3.	Nitric acid, approximately double normal.
	Grms.	Cc.	Cc.
5—10	0·6	36	20
1·5—5	1·8	96	26
0·25—1·5	3·6	186	35

The Analysis.

Select a Kjeldahl flask of 400 to 500 cc. capacity and having a neck 20 to 25 cm. long. Introduce into it the chloride-bromide mixture, add the potassium iodate solution and the nitric acid, and enough water to bring the volume to 200 or 250 cc. Support the flask at an angle of about 30° from the vertical, resting on a hole about 2½ inches in diameter, in a square of heavy asbestos board. The latter is of course intended to deflect the hot flame gases from the sides of the flask. The neck acts as a reflux condenser, returning to the flask traces of hydrochloric acid which might otherwise escape when the volume of the liquid is reduced to its minimum. Heat to gentle boiling with a Bunsen flame. It is advantageous, but not by any means necessary, to begin this operation near the close of a day's work, and after boiling for five minutes to allow the solution to stand over-night. The reaction goes on while standing, and thus shortens the actual period of boiling. In any case, boil down to a volume of about 90 cc. This point should be permanently marked on the outside of the flask in such a way as to correspond to its slope. When the amount of chloride is small, the volume may be reduced to 60 cc. without measurable loss, but in general the 90 cc. mark should not be passed. The boiling ought to go on at such a rate that thirty to forty minutes are required. The solution is now usually perfectly colourless, and only traces of bromine remain. Add 100 cc. of water, and continue the boiling until 50 cc. have passed off. The escaping vapour may now be tested with fluorescein paper, held across the mouth of the flask for five minutes. If no change of colour from yellow to orange occurs, the final test may be made. For this purpose, pass the escaping steam, with the help of a clean rubber stopper and narrow bent glass tube, through 10 cc. of a 2 per cent solution of potassium iodide to which enough decinormal hydrochloric acid has just been added to impart a faint acid reaction, in a test-tube, until the solution has become hot (about forty seconds). If this liquid shows no yellow colour when held against a white surface the bromine may be regarded as expelled. (It is hardly necessary to say that the iodide must be pure and able to stand heating under the conditions prescribed, without any colouration, when bromine is absent). This test is more delicate than fluorescein or than sodium bicarbonate solution faintly tinted with indigo.

When the bromine is all expelled, add, without interrupting the boiling, 1·0 to 1·50 cc. of a 25 per cent solution of phosphorous acid. Continue the boiling till all iodine is

driven off, as shown by the colour, and five minutes longer. This requires about ten minutes in all. At no time may the volume be allowed to become less than 90 cc. (except in the case previously mentioned, when the total amount of chlorine is small, a few mgrms.).

To the water-white and cooled solution in the flask add a moderate excess of twentieth or of fiftieth normal silver nitrate solution (according to the amount of chloride present), then a fragment of the best filter-paper, and shake violently till the paper is reduced to pulp. Filter, wash, add 5 cc. of 10 per cent ferric nitrate solution, and titrate after Volhard with twentieth or fiftieth normal sulphocyanate till coloured, and then back with the silver solution. The end-point can always be more exactly hit in this direction.

The freedom from chlorine of all reagents should be controlled. The standard potassium or ammonium sulphocyanate will not give a sharp end reaction if it contains chloride. It may be tested in the same way as a bromide, *i.e.*, decomposing by boiling with nitric and iodic acids, &c.

The fifth normal potassium iodate solution contains 7·138 grms. of the purest re-crystallised salt to the litre. If preferred, a normal solution may, of course, be employed instead.

The freedom of this salt and of the other reagents from chlorine may best be determined by a blank analysis on 2 grms. of the potassium iodide, using the regular amounts of iodate, nitric acid, and phosphorous acid. Phosphorous acid is the only reagent which cannot be easily found free of chlorine, and the amount used is so small that a trace of chlorine in it does not, as a rule, matter much, as the error so introduced is usually less than 0·01 per cent.

The following analyses of mixtures of known composition will serve to show the degree of accuracy to be expected from the method. A nearly pure potassium bromide, containing 0·025 per cent of chloride, was mixed with varying amounts of potassium chloride, and the mixture then analysed by the method described. The first column gives the weight in grms. of the bromide taken; the second, the weight of potassium chloride added (in the form of a standard solution); the third, the total amount of chloride present; the fourth, the number of cc. of standard silver solution consumed; the fifth, the weight of potassium chloride found; the sixth, the percentage of chloride actually present; the seventh, the percentage of chloride found.

Bromide taken.	Chloride added.	Total chloride.	Silver solution. N/50.	Chloride found.	KCl present.	KCl found.
Grms.			Cc.		Per cent	Per cent.
3·6000		0·0009	0·60			0·025
3·6000	0·0361	0·0370	24·55	0·0366	1·077	1·06
3·6000	0·0722	0·0731	48·82	0·0728	1·991	1·982
			N/20.			
3·6000	0·1083	0·1092	29·32	0·1094	2·945	2·950
3·6000	0·1444	0·1453	39·13	0·1459	3·880	3·896
1·8000	0·1444	0·1449	38·93	0·1452	7·453	7·467

Further, a mixture was made by me of pure potassium chloride and of a potassium bromide containing 0·07 per cent of chloride, both pulverised, dried at 150°, and then thoroughly incorporated in such proportion that the product contained 3·95 per cent of chloride. Portions were then given to three chemists for analysis with no further information beyond the fact that the amount of chloride was between 1·5 and 5·0 per cent. Only one of these chemists had used the method before. They reported the following results:—

Chemist "C" reported 3·93 per cent of chlorine; "S" reported 3·98, and in a duplicate 3·88, with the remark that he thought this "too low, since the evaporation has been carried much too far"; "A," 4·02; "L," 3·96 per cent. There is no doubt that with practice even closer results than this set of analyses indicates can be regularly obtained.

Evidence of this is given by the analyses of crude bromine reported below.

The method has now been in constant use in the laboratory of the Mallinckrodt Chemical Works for six or eight months with uniformly satisfactory results.

Determination of Chlorine in Crude Bromine.

Crude bromine (of American origin) contains chlorine varying in amount from 1 to 13 per cent or even more, a very minute amount of iodine, a small quantity of water (not far from 0·05 per cent), brominated organic matters derived from tallow, and small amounts of tar formed by the action of bromine on coal-tar. Some samples contain an easily recognisable quantity of bromoform, which is left as a nearly colourless liquid when 25 or 50 cc. of the bromine are allowed to evaporate in a current of air.

The percentage of chlorine may be determined by converting the sample quantitatively into a mixture of chloride and bromide by dissolving in caustic soda, evaporating to dryness, fusing in the presence of a little sugar-charcoal, then analysing the melt by the process already given for bromides.

A much shorter, more convenient, and at the same time somewhat more accurate method, consists in treating the weighed sample of crude bromine with a solution of an alkali iodide insufficient to react with all the bromine, but more than sufficient to retain all the chlorine in the sample. No chlorine escapes from this mixture on boiling. The amount of salt to be handled is less than would be the case if all the bromine were converted into bromide, and, consequently a larger sample can be taken, which contributes materially to the accuracy when the percentage of chlorine is very low—for example, a few tenths or even thousandths per cent.

Before describing working details of this procedure, it is appropriate to draw attention to certain precautions necessary to observe in securing samples of the crude bromine for analysis and in handling them when obtained. Special precautions are imposed on account of the ease and rapidity with which the composition changes by evaporation of the chlorine. I have satisfied myself by actual analyses that it is impossible to pour bromine from one bottle to another without a very appreciable diminution in chlorine percentage occurring. The ordinary temperature and an ordinary bromine of from 4 to 6 per cent of chlorine are here understood. A bottle containing about 600 grms., closed with a badly-ground glass stopper, stood in the laboratory about a month, during which period it was opened two or three times just long enough to withdraw a sample for analysis. The chlorine gradually fell from 6·44 per cent to 5·58. Another sample was allowed to stand in a narrow tall cylinder till, by evaporation, its volume was reduced from 50 to 39 cc. This resulted in a diminution of chlorine from 6·2 to 3·4 per cent.

These facts are recorded in order to emphasise the propriety of drawing samples by means of a suitable special pipette, without suction, from beneath the bromine layer, and of avoiding under all circumstances pouring bromine to be analysed from one receptacle to another. When the amount of chlorine exceeds 2 per cent, it is well to cool the bromine bottle in ice-water before taking the sample.

A suitable form of pipette for compositing samples can be made from an ordinary 5 cc. pipette by passing through the upper stem a glass rod which at its lower end is ground to fit perfectly the lower opening of the bulb. The lower stem is removed and replaced by a delivery nozzle only 2 or 3 mm. long, into which the ground joint extends so as to leave no dead space. In the centre—or, as the case may be, in the upper part—of the bulb a hole about 3 or 4 mm. in diameter is made. In use, the valve is lifted and the instrument is plunged quickly far below the surface of the bromine. The air escapes from the side opening, and the filling is very rapid. The pipette is now closed by

depressing the rod, and is raised above the liquid for a few seconds. It thus drains on the outside while inside the bottle. It is now quickly lifted and permitted to empty partially, or wholly, either into the chilled container used for compositing, or into the weighed glass-stoppered flask containing potassium iodide solution. For the latter purpose a pipette of similar construction but smaller size is preferable. The Lunge-Rey and other forms of weighing pipettes have also been used for this purpose in this laboratory with success. Their disadvantage is that it has proved to be impossible to get stopcocks so perfectly ground on these instruments as to hinder the escape of more or less bromine into the balance case. If used, graphite is the only permissible lubricant. It is impossible to entirely avoid loss of chlorine during the manipulations, even with every precaution. Since this loss does not by any means increase in proportion to the weight of bromine taken, it follows that a relatively large amount should be weighed, and the solution at a subsequent stage subdivided for analysis, if the quantity of chlorine present is too large for direct titration.

The Process.—Introduce about 3 grms. of the bromine, accurately weighed, or more if the chlorine content is below 0·5 per cent, into a solution of 2 grms. of potassium iodide in 50 cc. of water contained in an Erlenmeyer flask with a well-ground stopper. In warm weather, flask and contents should be previously cooled in ice. Quickly insert the stopper, and shake. Transfer to a 400 cc. Kjeldahl flask, disregarding the escape of vapours of iodine and bromine, and, after rinsing add 60 cc. of fifth normal potassium iodate (or 12 cc. of the normal solution), 24 cc. of nitric acid, and water to make about 250 cc. Proceed from this point precisely as in the analysis of a bromide (see above). Of course, when the solution is ready for titration, an aliquot part should be taken if the amount of chlorine is so large as to make this step desirable.

The bromine may for many practical purposes be determined sufficiently well by difference, since the total quantity of impurities other than chlorine is usually much less than 1 per cent.

If accuracy is desired, the total free bromine and chlorine should be determined by an iodometric titration, the weighed substance being dissolved in a considerable excess of potassium iodide solution, and the liberated iodine titrated after feeble acidification. Correcting the volume of thiosulphate here required by that equivalent to the chlorine found, the difference gives the free bromine.

It is obvious that the accuracy of the method described for the determination of chlorine in bromine, or of any other process for this purpose, cannot be shown by analyses of known mixtures, since the errors in preparing such a mixture must far exceed the analytical errors. It is only possible to show the agreement of duplicate analyses and the concordance of the analytical results with physical properties. The latter will be taken up in another paper.

As illustrative of the former, I take at random several analyses out of a large number made by Dr. H. A. Carlton.

Sample.					
6706	Found per cent of Cl	2·445	2·380		
6806	„ „	2·069	2·072	2·052	2·32
1220 dry	„ „	4·439	4·422		
1220 saturated with water		4·407	4·401		
1220 dried again		4·438	4·461		
5406		8·55	8·57		
424		5·00	4·98	5·04	5·06

It is confidently believed that the methods here described for the determination of chlorine in bromine and bromides are a practical solution of this old analytical problem, suitable for routine analyses of either technical or scientific character, and adapted to replace the indirect methods.

It is a pleasant duty here to express my obligations to Dr. Carlton for his able assistance in the work.—*Journal of the American Chemical Society*, xxix., No. 3.

NOTICES OF BOOKS.

Annual Report of the Minister of Mines for the Year ending December 31st, 1906. Victoria, B.C.: Richard Wolfenden. 1907.

This volume contains the Annual Report of the Provincial Mineralogist, Mr. W. F. Robertson, upon the mining industry in the province of British Columbia for last year, and gives tables showing the total mineral output and the actual mineral production. For purposes of comparison, summaries of the productions of the last four years are also included. The curves showing the value of the total production, lode mines, and coal and coke make it easy to form an accurate idea of the progress of the industry, while the detailed and excellently illustrated accounts of the mining operations of the various districts of the province are drawn up in such a way as to provide the maximum of reliable information.

Post's Chemisch-Technische Analyse. ("Post's Technical Chemical Analysis") Vol. I., Part III., and Vol. II., Part II. Third Edition. Edited by Prof. Bernhard Neumann. Braunschweig: Friedrich Vieweg und Sohn. 1907.

The third part of Volume III. of the third edition of this excellent treatise on analytical chemistry gives concise accounts of the most reliable and convenient laboratory methods of estimating iron, written by Prof. Lebedur, and other metals, by the general editor. The methods chosen for description include only those which give satisfactory results, and the experimental details are given in full, so that the student should find no difficulty in performing analyses with little or no help from the teacher. Electrolytic processes are included, and a short section is added upon the determination of some important metallic salts. Volume II., Part II., deals equally efficiently with the carbohydrates, alcoholic beverages, yeast and vinegar, and allied products.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlv., No. 11, September 9, 1907.

Alloys of Cobalt and Tin.—F. Ducelliez.—The following table gives a *résumé* of the results of the author's work upon alloys of cobalt and tin:—

Percentage of tin.	Composition of alloys.	Definite alloys isolated.	Physical properties.	
0	Co and Co_3Sn		Brittleness increases.	Magnetic alloys.
57·65		Co_3Sn_2	D = 8·862, limit of magnetism.	
	Co_3Sn_2 and CoSn		Very brittle.	
66·77		CoSn	D = 8·950.	Non-magnetic alloys.
85	CoSn and Sn		Becoming less hard & brittle.	
100			Malleable alloys.	

MEETINGS FOR THE WEEK.

Wednesday, 16th.—Microscopical, 8. "A New Prismatic Microscope Ocular" and "On Ghost Images seen in the Secondaries of *Coscinodiscus asteromphalus*," A. A. C. E. Merlin. "Systematic Exposure with Transmitted Light in Photomicrography," by A. Letherby.

Friday, 18th.—Chemical, 9. (Extra Meeting). Prof. Emil Fischer, F.R.S., will deliver the Faraday Lecture, entitled "Organic Synthesis and its Relation to Biology."

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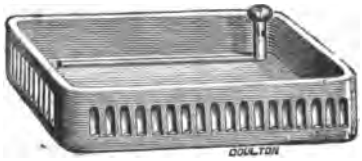

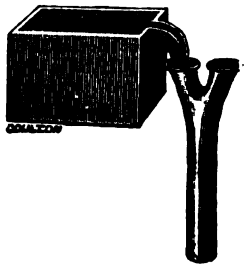

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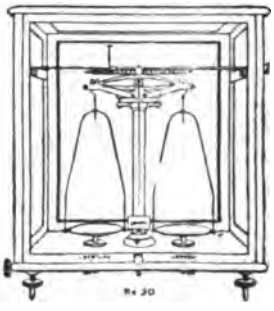

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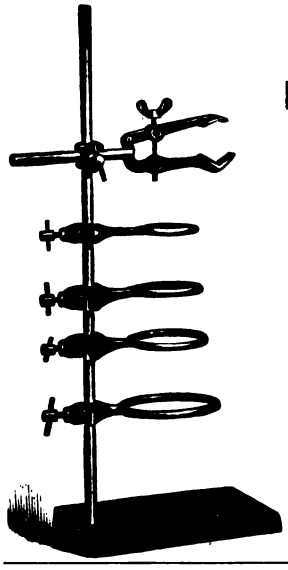

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THE CHEMICAL NEWS.

VOL. XCVI., No. 2499.

VULCANISATION TESTS WITH PLANTATION RUBBER.

(SECOND COMMUNICATION).

By CLAYTON BEADLE and HENRY P. STEVENS.

IN a previous paper which appeared in the CHEMICAL NEWS (vol. xcvi., p. 37) we published the results of a number of vulcanisation tests with plantation rubbers. These experiments were carried out with a view to ascertaining the value to the manufacturer of plantation rubber as compared with the ordinary brands on the market. For this purpose we not only vulcanised and tested samples of plantation rubber, but the results we obtained were compared with similar tests made on the standard rubber, viz., hard-cure para, which was washed, dried, and subsequently vulcanised alongside of the plantation rubber.

The results of our tests showed that the plantation rubber experimented with gave better figures than the hard-cure para.

These researches have aroused considerable interest among planters, manufacturers, and others, and certain criticisms were offered in a recent issue of the *Indiarubber Journal* (Sept. 9, 1907, p. 321), to the effect that the hard-cure para was subjected by us to a more severe treatment in the process of washing than would have been the case in a rubber works, and that in consequence the nerve of the rubber had been gravely affected, while, on the other hand, the plantation rubber was not washed, but mixed straight away and vulcanised, and was therefore treated under more favourable conditions, and consequently, as might have been expected, yielded better results.

As we have since pointed out, however, it is obvious that, on a manufacturing scale, it would be necessary to wash and dry the hard-cure, and our results are all the more practical for the reason that we followed the manufacturers' example; but as properly prepared plantation rubber should not require this treatment in the factory we did not subject it to such treatment in the laboratory. Hence any disadvantages attaching to the treatment of the hard-cure in our experiments would also apply in practice, nor do we think that such treatment was more severe in our tests than it would have been on a manufacturing scale.

Since our previous communication we have been steadily at work accumulating vulcanising data, and we have now concluded a series of vulcanising tests with hard-cure which had been washed and dried by a manufacturer, and was therefore in the exact condition in which it would be used by the manufacturer himself. In this way we were able to meet the criticism above referred to, and to eliminate any disturbing influence due to the use of laboratory apparatus for washing the hard-cure.

Table I. gives the analysis of hard-cure para washed and dried as supplied by a manufacturer, and for purposes of comparison we have placed alongside a recent analysis of plantation rubber.

TABLE I.

	Hard-cure para, after washing and drying by manufacturer.	Plantation rubber as received by manufacturer.
Moisture	0·5	0·6
Protein	2·0	1·3
Resin	2·9	3·9
Ash	0·6	0·3
Caoutchouc (by diff.) ..	94·0	93·9

The results of this series of tests are given in Table II., and, so far from proving superior to vulcanised plantation rubber, the hard-cure washed and dried by the manufacturer yielded lower figures for tensile strength than the hard-cure which we had washed and dried in our own laboratories.

TABLE II.

Vulcanisation reference number.		Tensile strength, in grms.	Elongation at rupture when original =1·0.	Elongation under a strain 1500 grms. when original =1·0.
203		1500	—	—
209		2046	14·4	14·3
205		2174	15·4	13·6
216	Q2	2121	13·8	12·8
265		2391	12·8	11·9
251		2682	13·9	12·2
207		2558	13·6	11·8
210		1977	13·4	—
214		2168	13·6	13·0
227		2675	13·7	11·5
225	S2	2808	13·7	10·7
250		2793	13·5	12·5
259		2872	13·5	10·9
256		2777	13·0	9·8
229	W2	2116	13·7	12·1
233		2531	13·8	12·8
270		2315	13·5	13·3 (*a*)
266	D3	2696	12·8	11·3 (*b*)
260		2886	13·2	11·4 (*c*)
257		2229	11·9	10·9 (*d*)

Duration of vulcanisation: (*a*) Three hours, (*b*) four hours, (*c*) five hours, (*d*) six hours.

These vulcanisations and tests were carried out as described in our previous communication. The letters referring to mixings and the numbers to vulcanisations. In the individual vulcanisations the time and temperature (or pressure) in the vulcanisation tests were varied so as to bring out the best results possible with each mixing. We give the results of all the vulcanisations made with these mixings, including those which yielded unsatisfactory results, as in a certain number of cases the samples were either somewhat over or under cured. But taking, in this way, a wide range of temperatures and curing for various periods, we gradually worked up from under-cured samples to those which were fully cured, finally carrying the series of tests to a point where the samples were obviously over-cured.

These vulcanisations include both long cures at comparatively low temperatures, as well as shorter cures at higher ones, and it is not therefore possible in most cases to arrange the samples in the order of the cure. However, in vulcanisations D3 the temperature in all cases was the same, the time only being varied. We are therefore able to note the progressive effect of the cure on the properties of the vulcanised rubber.

The results obtained are instructive: D3 270 heated for three hours is obviously under-cured, the cure being insufficient to bring out the full tensile strength, and the sample is somewhat "soft," showing an elongation of 13·3 with a load of 1500 grms. Vulcanisation for two hours longer is sufficient to develop the highest tensile strength obtained, the elongation with a load of 1500 grms. being 11·4. On vulcanising for six hours the sample is over-cured, the tensile strength falls again, at the same time the product gets somewhat short or brittle and the elongation (10·9) is less than in the other cases. On averaging up the tensile strength of those samples in which the conditions of vulcanisation have brought out the greatest tensile strength, it is apparent that the resulting figures obtained are much lower than those obtained in the previous tests on vulcanised hard-cure para, which had been carefully washed and dried by ourselves, and of course are considerably lower than those obtained with the vulcanised plantation rubber.

We are extending our researches on the vulcanising qualities of crude rubbers in other directions, and are at present engaged in instituting a comparison between the different forms of plantation rubbers at present on the market with a view of ascertaining which form—that is to say, whether sheet, biscuit, block, crepe, &c.—yields the strongest and most resilient product on vulcanisation.

So far as we have gone, the results obtained with different forms of plantation rubber differ materially from one another, and it would appear that in future, when this difference in behaviour is better recognised, planters will require to consider carefully whether the form in which they are shipping their rubber is that which yields the best results to the manufacturer.

ON THE CALCULATION OF THERMO-CHEMICAL CONSTANTS.

By H. STANLEY REDGROVE, F.C.S.

Molecular Heats of Formation of the Hydrocarbons.

THE author has already shown that his method of calculation may be applied with great accuracy to the molecular heats of combustion of the hydrocarbons (CHEMICAL NEWS, xcv., 301).

The following paper deals with molecular heats of formation.

The constants that were found necessary in the consideration of physico-chemical properties in general, and defined (CHEMICAL NEWS, xcv., 193), can be used here; but as they will have different specific significations from that with which they were employed in the consideration of molecular heats of combustion, it will be advisable to dash them when employed in the consideration of molecular heats of formation in order to avoid confusion.

Consider the case of the general hydrocarbon :—

$$nC+2(n+1-a-2b-p)H+(n+p-a-b-1)L_1+aL_2+6L_3.$$

The heat of formation of 1 molecule of this hydrocarbon from carbon molecules and hydrogen molecules is the algebraic sum of the following heats :—

1. The heat due to the dissociation of a sufficient number of carbon molecules to provide n isolated carbon atoms.
2. The heat due to the dissociation of $(n+1-a-2b-p)$ hydrogen molecules, H_2.
3. The heat of formation of $2(n+1-a-2b-p)$ C.H links.
4. The heat of formation of $(n+p-a-b-1)$ C.C links.
5. The heat of formation of a C=C links.
6. The heat of formation of b C≡C links.

The coefficients of Heats 2 and 3 are always in the ratio 1 : 2, therefore their algebraic sum can be considered as one constant.

Dealing with grm.-molecular weights and using the notation already adopted :—Heat 1 = nC' cals. Σ Heats 2 and 3 = $2(n+1-a-2b-p)H'$ cals. Heat 4 = $(n+p-a-b-1)L'_1$ cals. Heat 5 = aL'_2 cals. Heat 6 = bL'_3 cals.

It should be noticed that $L'_1 = -L_1$, $L'_2 = -L_2$, $L'_3 = -L_3$.

It has already been proved in general that the values of these constants are unobtainable at our present state of knowledge, but the values of the "fundamental constants" $\alpha'(=C'+4H')$, $\beta'(=2H'-L'_1)$, $\gamma'(=4H'-L'_2)$, and $\delta'(=6H'-L'_3)$ may be calculated in a similar manner to those for molecular heats of combustion.

In Table 1A will be found the molecular heats of formation (from molecules of amorphous carbon and hydrogen molecules), corrected for constant volume, given by Thomsen ("Thermo-chemical Researches," 1906, German Edition). The values of the "fundamental constants" calculated from these results are : — $\alpha' = 21{\cdot}2$ cals., $\beta' = 15{\cdot}0$ cals., $\gamma' = 46{\cdot}0$ cals., and $\delta' = 89{\cdot}5$ cals. (see Note).

[NOTE.—The fundamental heat of formation constants may be more readily calculated from the heat of combustion constants as follows :—

C' = Heat combustion 12 grms. amorphous carbon at constant volume $-C$.

$\therefore C' = 97{\cdot}0$ cals. $- C$.

$2H'$ = Heat combustion 2 grms. hydrogen at constant volume $- 2H$.

$\therefore 2H' = 67{\cdot}5$ cals. $- 2H$.

$\therefore \alpha' = C'+4H' = 97{\cdot}0$ cals. $+ 2(67{\cdot}5)$ cals. $- (C+4H)$ $= 232{\cdot}0$ cals. $- \alpha = (232{\cdot}0 - 210{\cdot}8)$ cals. $= 21{\cdot}2$ cals.

Also, $L'_1 = -L_1$, $L'_2 = -L_2$, $L'_3 = -L_3$.

$\therefore \beta' = 2H' - L'_1 = 67{\cdot}5$ cals. $- (2H - L_1) = 67{\cdot}5$ cals. $- \beta = (67{\cdot}5 - 52{\cdot}5)$ cals. $= 15{\cdot}0$ cals.

Similarly for γ' and δ'].

The molecular heats of formation of the hydrocarbons have been calculated from these values, and are given in the table. The identical conclusions can be deduced from a consideration of these as were deduced from a consideration of molecular heats of combustion. Thus, $T_2 = L_2 - 2L_1 = 2L'_1 - L'_2 = \gamma' - 2\beta' = 16{\cdot}0$ cals. (the value found before), &c.

The molecular heats of formation, however, being in general much smaller quantities numerically than the corresponding molecular heats of combustion, the percentage error in calculating the former is necessarily much larger than in calculating the latter. The actual errors are of the same magnitude in each case, the only considerable one being in the case of di-isopropyl as before.

In conclusion, it would not be inappropriate to refer to Mr. Thomlinson's alleged thermo-chemical equivalents.

In calculating his constants for C and H (CHEMICAL NEWS, xciii., 37) from which the others are derived, Mr. Thomlinson treats CH_4 as if it could be regarded as made up of two factors, whereas it is made up of three; either Mr. Thomlinson has assumed the value of the C.H link to be zero, or else he employs his H constant to mean the algebraic sum of the heat of dissociation of ½ grm. molecular weight hydrogen, and the heat of formation of the corresponding number of C—H links in a similar manner as myself, but in this latter case the H constant is only applicable to hydrogen combined with carbon (to which I have confined myself), whereas Mr. Thomlinson uses it in general.

A further assumption is made when we come to ethane, for here the value of the C.C link is also supposed to be zero.

These assumptions I have already pointed out to be quite unjustifiable.

Mr. Thomlinson would doubtless reply that he was justified in making these assumptions, because the value of propane calculated from his figures is correct. That this fact does not confirm his assumptions is evident at once from a consideration of indeterminate equations.

To simplify matters we will consider for the time being only the hydrocarbons, so that the treatment of CH_4 as if it depended on two factors only is allowable. We then have two equations, $C'+4H' = 21{\cdot}750$, $2C'+6H'+L'_1 = 28{\cdot}560$ (I use Mr. Thomlinson's figures, which are uncorrected).

$3C'+8H'+2L'_1 = 35{\cdot}110$* is not another independent equation, because it can be derived from the first two :— $3C'+8H'+2L'_1 = 2(2C'+6H'+L'_1) - (C'+4H')$. But two equations involving three unknowns are indeterminate; now the property of such a set of eqations is such that, whatever value I choose to give to one unknown, I can always find values for the other unknowns to satisfy all the equations. Mr. Thomlinson chooses to assume $L'_1 = 0$; with equal justification I could assume it to be any number; to give an actual example I will assume $L'_1 = 100$.

Then, $C'+4H' = 21{\cdot}750$, $2C'+6H'+100 = 28{\cdot}560$, whence solving simultaneously $C' = -208{\cdot}130$, $H' = 57{\cdot}470$.

Using Mr. Thomlinson's method of "confirmation" we get $3C'+8H'+2L'_1 = 35{\cdot}370$ (*) as on his assumption.

* In Mr. Thomlinson's paper the decimal point has been shifted, I suppose by a printer's error.

TABLE I.A.—*Hydrocarbons.*

1. Hydrocarbon.	2. Formulæ.	3. Formulæ.	4. M.H.F. (constant volume). Thomsen.	5. M.H.F. calculated.	6. Difference between Cols. 4 and 5.
			Cals.	Cals.	Cals.
Methane	$C'+4H'$	a'	+21·2	+21·2	0·0
Ethane	$2C'+6H'+L'_1$	$2_1'-\beta$	27·4	27·4	0·0
Propane	$3C'+8H'+2L'_1$	$3a'-2\beta$	33·4	33·6	+0·2
Trimethylmethane	$4C'+10H'+3L'_1$	$4a'-3\beta$	40·1	39·8	−0·3
Tetramethylmethane	$5C'+12H'+4L'_1$	$5a'-4\beta$	45·0	46·0	+1·0
Di-isopropyl	$6C'+14H'+5L'_1$	$6a'-5\beta$	57·6	52·2	−5·4
Ethylene	$2C'+4H'+L'_2$	$2_1'-\gamma$	−3·3	−3·6	−0·3
Propylene	$3C'+6H'+L'_1+L'_2$	$3a'-\beta-\gamma$	+2·1	+2·6	+0·5
Trimethylene	(c) $3C'+6H'+L'_1-T$	(c) $3a'-3\beta'-T$	−4·6	−4·5	+0·1
iso-Butylene	$4C'+8H'+2L'_1+L'_2$	$4a'-2\beta-\gamma$	+8·9	+8·8	−0·1
iso-Amylene	$5C'+10H'+3L'_1+L'_2$	$5a'-3\beta-\gamma$	16·7	15·0	−1·7
Diallyl	$6C'+10H'+3L'_1+2L'_2$	$6a'-3\beta-2\gamma$	−11·6	−9·8	+1·8
Acetylene	$2C'+2H'+L'_3$	$2a'-\delta$	−47·8	−47·1	+0·7
Allylene	$3C'+4H'+L'_1+L'_3$	$3a'-\beta-\delta$	−40·5	−40·9	−0·4
Dipropargyl	$6C'+6H'+3L'_1+2L'_3$	$6a'-3\beta-2\delta$	−97·2	−96·8	+0·4
Benzene	(a) $6C'+6H'+3L'_1+3L'_2$	$6a'-3\beta'-3\gamma'$	−13·7	−55·8	−42·1
	(b) $6C'+6H'+9L'_1$	$6_1'-9\beta'$		−7·8	+5·9
Toluene	(a) $7C'+8H'+4L'_1+3L'_2$	$7a'-4\beta'-3\gamma'$	−5·3	−49·6	−44·3
	(b) $7C'+8H'+10L'_1$	$7a'-10\beta'$		−1·6	+3·7
Mesitylene	(a) $9C'+12H'+6L'_1+3L'_2$	$9a'-6\beta'-3\gamma'$	−2·4	−37·2	−34·8
	(b) $9C'+12H'+12L'_1$	$9a'-12\beta'$		+10·8	+13·2
Pseudocumene	(a) $9C'+12H'+6L'_1+3L'_2$	$9a'-6\beta'-3\gamma'$	−1·6	−37·2	−35·6
	(b) $9C'+12H'+12L'_1$	$9_1'-12\beta'$		+10·8	+12·4

(*a*) Kekulé's formulæ.

(*b*) Ladenburg's or Claus's formulæ, without subtracting the value due to tension; in the case of Ladenburg's the value of this intramolecular tension is greater than 46·2 cals.

(*c*) T is the thermal value of the intramolecular tension in the trimethylene molecule, and has been found to be equal to 23·1 cals. It should be borne in mind that whilst in calculating molecular heats of combustion this value is to be added; in calculating molecular heats of formation this value must be subtracted.

So that if Mr. Thomlinson has shown that the values are $C' = -8{\cdot}130$, $H' = 7{\cdot}470$, and $L'_1 = 0$; with equal logic I have shown them to be $C' = -208{\cdot}130$, $H' = 57{\cdot}470$, $L'_1 = 100$. This, I think, settles the question, and clearly shows that the true values are unknown and indeterminate.

This is only a particular case of the general proof I have given (CHEMICAL NEWS, xcv., 193).

It should also be noticed that Mr. Thomlinson has to make a very large number of assumptions, without any justification, to bolster up his hypotheses. Thus we have such weird formulæ proposed as O≡O and $(OH)_3P$—O (*i.e.*, tetravalent phosphorus and penta- and monovalent oxygen are assumed); in fact, a very loose conception of valency seems to permeate his papers.

For instance, what does this mean (CHEMICAL NEWS, xcv., 50):—"If in nitrous oxide, N_2O, oxygen be represented as pentavalent, but with the difference that in the structural formula shown below, in which nitrogen is trivalent, there is one oxygen bond of valency which forms a central union in the molecule, without affecting the trivalency of nitrogen . . . $N\equiv \gtrless O \lesssim N$"?

It appears, when simplified, to reduce to the statement $2 = 1$!

Even with all this bolstering up, Mr. Thomlinson's calculated values are not on the whole in good agreement with the experimental results, as reference to his papers make evident.

The Polytechnic, Regent Street, W.

[NOTE.—The author's attention has recently been called to a paper by Thomsen (*Zeit. Phys. Chem.*, 1905, li., 657) in which a method of calculating the heats of combustion of hydrocarbons is employed, resembling somewhat the author's method. It is, perhaps, unnecessary to state that the short criticism in CHEMICAL NEWS (xcv., 301) did not apply to this method].

THE ARTIFICIAL REDISTRIBUTION OF THE METALS.

By H. M. ATKINSON.

ALTHOUGH man's activities are confined to a thin film of the earth's sphere, yet the total effect of these, acting as they have been for some thousands of years, must have produced a considerable effect on the distribution of the elements, the metals especially. It amounts to a redistribution, for the accumulation, *e.g.*, of the noble metals, is not a permanent one. For, leaving out of account the atomic changes which gold, &c., may undergo, these metals are subject to wear—a sort of human denudation. This takes place chiefly in civilised countries, and the result of this denudation is a diminishing of the useful or active mass of metal, and the transference of this amount to the deposit settling at the mouths of rivers, or a little beyond them. The gold, silver, &c., thus carried off must be in excessively fine particles, so small that their weight is not materially different from the particles of sand, clay, &c., carried along with them; so that a more or less homogeneous mixture would be laid down.

Thus the metal is lost; for even supposing earth movements laid bare these deposits sufficiently thick to work, the percentage of gold would be so small that it would not pay our descendants to work them, at any rate with modern processes of extraction. The noble metals then are being extracted from the ancient rocks, their chief source where their local concentration is comparatively large, and are laid down again in new rocks where their concentration will be very small.

Tin seems to offer a good illustration. Tin oxide has a large concentration in a few scattered places on the earth's surface. It is mined, reduced, and spread pretty uniformly over the world as tin sheet. Rusty old tins are an eyesore on the refuse heaps round all towns. The tin gets oxidised, and ultimately the particles are washed down into the rivers, and by them spread over the sea-bottom. Here

also a more or less uniform distribution of tin is taking place, and a lowering of the concentration.

As de Morgan said, "The second instance begins the induction." This leads me to my thesis :—

Man's effect on the distribution of the metals tends to the formation of a uniform deposit.

The older rocks contained patches or veins of great richness in some metals and absolutely devoid of others; the new rocks will be poor in all. Somewhat similar to the destiny of energy, *i.e.*, uniformity.

I do not overlook the fact that other circumstances may be at work countering this effect. The "*Erz-lagern*" have probably been formed by solution; the long infiltration of solutions, very dilute it is true, formed under the great pressures in the earth's crust. But these counter effects would not be so powerful in ocean or sea deposits when forming.

Could any experimental evidence be obtained? The difficulty in the way would be great. The mere getting of a sample for analysis, sea-mud beyond the Mersey bar, *e.g.*, would be easy enough; the analysis for minute traces of the common metallic elements would be difficult, as traces of gold have been found in sea-water itself.

There are many side issues from the main theme. Is the composition of the sea itself being altered? The effect of modern manufacturing processes might seem to indicate an accumulation of soluble chlorides; an up-to-date farmer sends a larger amount of potash and lime salts to the common sink than before; thus the Stassfurth K concentration is lowered to the marine K concentration.

THE QUANTITATIVE SYNTHESIS OF ARGENTIC NITRATE, AND THE ATOMIC WEIGHTS OF NITROGEN AND SILVER.*

By THEODORE WILLIAM RICHARDS
and
GEORGE SHANNON FORBES.

(Concluded from p. 183).

The Purity of the Fused Argentic Nitrate.

THE first impurity for which search was made was air. While crystals obtained from solution, although always containing solvent, may be supposed to be free from air, the fused material cannot without question be assumed to be free from this impurity. The only manner of approaching this question seems to be to fuse the salt a second time in a vacuum, in order to detect a possible loss of weight. This Stas did in a single case, with a negative result. Nevertheless, a single experiment, even of Stas's, does not carry with it much weight; therefore the test deserves repetition.

This was carried out in the present case without great difficulty on five of the preliminary determinations. The flasks containing the argentic nitrate which had been fused for an hour in air were lowered into mammoth test-tubes —long tubes of soft glass 4·5 cm. in diameter—sealed at the lower end and scrupulously clean. A hood was placed over the mouth of the flask to prevent fragments of glass from entering, and the tube was drawn down in two large converging blast flames. A glass tube was fused on and connected with an efficient mechanical hand-pump; several exhaustions, followed by admission of dry air, excluded all moisture. Finally, the system was reduced to 2 mm., and sealed, and heated to 210°. After having been maintained in a state of fusion in the dark for half-an-hour, the salt was cooled in the usual cautious fashion, and air was admitted very slowly. The flask was placed in a desiccator over-night, and weighed. The product was always slightly discoloured, indicating decomposition, but showed no serious loss in weight.

The Effect of Fusion in Vacuum.

Determination. number.	Original weight.	Weight after fusion.	Change.
	Grms.	Grms.	
1.	8·04489	8·04477	−0·00012
2.	8·75813	8·75810	−0·00003
3.	8·54170	8·54170	0·00000
4.	9·87850	9·87837	−0·00013
9.	10·76381	10·76374	−0·00007

Forty-five grms. of salt lost in all 0·00035 grm. This is less than 1 part in 100,000, and may safely be referred to the trace of decomposition indicated by the pale brownish coloration. Not only is it reasonable to suppose that but little air is dissolved (for according to the law of Henry nearly all of it should have been expelled by this treatment), but also one is led to infer that very little water remains to be expelled. This matter is not, however, so simply settled; the final testing of it cost much labour.

It has been ordinarily assumed that water is entirely expelled from crystallised or evaporated salts upon fusion. This is in all probability the case with sodic and potassic chlorides, and other salts which fuse at high temperatures and show little affinity for water. Whether or not this was the case with argentic nitrate, which at 210° is miscible with water in all proportions, was a question which required experimental investigation.

Besides the conservation of weight on fusion in a vacuum another argument may be adduced to show that most of the water has been driven out. The combining weight of argentic nitrate seems to be nearly independent of the time of its fusion in a current of dry air, as is shown by the following table :—

Determination.	Time kept in fusion.	Weight of $AgNO_3$ formed from 100 parts Ag.
14	15 minutes	157·481
9, 10, 11, 12, 13	1 hour	157·480
15	3 hours	157·480

It should be stated that the last residue was slightly discoloured, and increased 0·00008 grm. upon a subsequent evaporation with water and nitric acid; hence a real loss of weight during the extra period of fusion is indicated; but this was probably due to decomposition of the salt rather than to escape of water; therefore the table bears out the contention stated above. In any case this loss amounts to much less than a unit in the last decimal place.

Ordinarily, in the past, the investigator has been satisfied with such an outcome, and has gone no further. But in in this case we were anxious to leave no stone unturned, and accordingly a drastic method of treatment was adopted, which permitted no trace of water to escape being weighed. This was to decompose completely the argentic nitrate by heat, and to pass the gaseous product of the decomposition through a weighed tube containing phosphoric oxide.

A hard glass combustion tube was bent and drawn out in the manner shown in Fig. 2, the space between C and D being packed with glass-wool. Into the space between B and C was then introduced about 50 grms. of argentic nitrate which had been crystallised from nitric acid, barely fused in porcelain, cooled, and pounded in a mortar. The tube was heated to 220° in an air-bath for an hour in a stream of dry air passed in through A. The argentic nitrate should now be in a condition somewhat comparable to that of the quantitative determination. Finally, a weighed pentoxide tube was attached at D, and the temperature raised to 500°, Yellow oxides of nitrogen came over, also a fine grey dust caused presumably by the bursting of bubbles of decomposing salt. After an hour the pentoxide tube was removed, swept out with air, and weighed again. A trace of the grey dust had been carried in, and suggested a slight gain in weight, but by no means enough to account for the great increase of weight, 0·012

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grm. This was finally traced to the adsorption of nitrous fumes by the pentoxide, 2 mgrms. being lost upon passing dry air over the tube for an hour, and the rest giving a very strong test for nitrous acid after being dissolved in water.

In the effort to eliminate this seriously disturbing effect, recourse was next had to spirals of copper gauze heated in a combustion tube, in order to abstract the oxygen from the nitric oxide, leaving only nitrogen. It is well known that metallic copper adsorbs hydrogen; hence the spirals were first superficially oxidised in a stream of dry air, and then reduced by pure dry carbon monoxide. This was generated by heating the purest oxalic and sulphuric acids of commerce together, the carbon dioxide being absorbed by a generous train of pure concentrated potash solution, and the monoxide dried first by a tower of concentrated sulphuric acid, with beads, and finally by two towers of pounded potash. The resulting copper should be above the suspicion of containing any considerable amount of hydrogen or moisture. The argentic nitrate was treated as before, and the decomposition was continued until traces of yellow fumes were noted coming past the copper. This meant that nitric oxide had been coming over for some time, since the last part of oxygen is harder to detach than the first. When swept out with air, the gas in the pentoxide tube turned yellow, but it was not then supposed that much nitric oxide could be absorbed by the pentoxide in so short a time. Nevertheless, nitrous acid was found upon solution, even although the gain in weight was only a third as great as before.

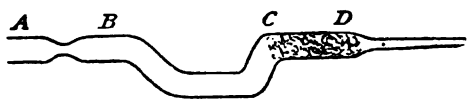

FIG. 2.—TUBE FOR DECOMPOSITION OF ARGENTIC NITRATE. (About one-eighth actual size).

Efforts were now made to reduce accidental water from rubber, &c. All joints were made to overlap, so that the rubber surfaces exposed to nitric oxide might be small, and large asbestos screens kept them from being overheated by the adjacent furnaces. Fresh sublimed pentoxide was used in the weighing-tube, which was carefully imitated as to volume and surface by a similar tube, to be used as a counterpoise in weighing; both were opened after coming to the temperature of the balance-room, wiped with a clean slightly damp cloth, and weighed by substitution. A substantial plug of glass-wool in the decomposition tube strained the gases before passing over the copper; it had been heated in the dry air to remove moisture.

To eliminate the possibility of water in the copper gauze and to test the apparatus, a blank run was made, removing the decomposition tube, and oxidising the copper with dry air. Here the pentoxide tube lost 0·0004 grm., a result which indicated no error in that part of the process.

It is not worth while to record the individual experiments by which the gradual improvements in apparatus and manipulation were tested, tiresome and time-consuming as these were in execution. By the time seven experiments had been performed, it was clear that the fused argentic nitrate could not contain over 0·004 per cent of water. Even of this small amount a part was undoubtedly due to nitric peroxide; for the copper gauze was not enough to effect a complete decomposition of the gases. Passing carbon monoxide through the apparatus while the decomposition was in progress lengthened the effective life of the reduced copper, but introduced other complications, and the addition of a second tube of hot gauze, a metre long, was still inadequate.

The next step was to secure a copper surface so large that all the nitrogen oxide resulting from the complete decomposition of 50 grms. of argentic nitrate could be removed, and this without increasing the complications of the apparatus. Powdered copper oxide looked promising as a source of this metal, but it must be made from pure materials to avoid the presence of detrimental impurities. Pure electrolytic copper (Merck) was dissolved in nitric acid, evaporated to dryness in porcelain, and very gradually ignited with constant stirring, to powdery oxide. A hard glass tube 30 cm. long and 3 cm. internal diameter was used to contain it; the ends were drawn down conveniently, and the oxide was reduced at a very moderate heat with carbon monoxide, prepared as usual, except that it was finally dried with pentoxide. Nearly 300 grms. of copper oxide were present; therefore the process was very tedious, since the gas had to pass through its purifying train at a moderate rate of speed. With this large mass of finely divided copper the glass-wool (from C to D in the diagram) was no longer necessary, therefore it was no longer used. No trace of powdered nitrate ever appeared beyond the copper.

A clean pentoxide tube, with glass stopcocks, was refilled with re-sublimed pentoxide and glass-wool; dry air was passed through for ten minutes to assure constancy. A duplicate tube was also prepared for a counterpoise, and extraordinary precautions were taken in protecting and weighing these tubes. As another precaution it seemed also expedient to prepare argentic nitrate nearly as pure as that used in the determinations for fear of hygroscopic nitrates, silicic acid, and ammonium salts, which would yield water when decomposed. A moderately pure salt was re-crystallised from nitric acid, filtered, precipitated with formate, washed free from ammonium salts, and fused on lime in the blast. The buttons were etched, and dissolved in freshly distilled nitric acid in Jena glass, and the salt was crystallised with ample protection against ammonia, dried centrifugally, and kept in a clean tight desiccator. There was no ammonia in this product. Before using it was fused in platinum.

In the first determination of this series the argentic nitrate was heated too hot (520°), and the gases came over so fast that the reduced copper was only superficially attacked; even so it was vastly more efficient than the gauze. Because, however, some nitric peroxide still escaped, this experiment also had to be rejected, a part of the 0·004 per cent impurity which it indicated being undoubtedly due to nitrous fumes.

The apparatus was now improved by sealing off the end (A) of the tube after the argentic nitrate had been fused for a long time in a current of dry air. Moreover, the last trace of rubber exposed to nitrous fumes was eliminated by providing an accurately ground joint between the decomposition tube and the copper oxide. The process was conducted so slowly at 490° that the argentic nitrate could be entirely decomposed to pure spongy silver without exhausting all the copper. Care was taken to have the very pure argentic nitrate in a state comparable to that used in the determinations. The salt after its preliminary treatment in platinum still contained a few crystals of unfused nitrate; accordingly, in the tube it was heated evenly at 220° with shaking to dislodge steam bubbles, exactly as the determinations had been. Under these conditions reliable results were obtained. In No. 25, a second weighed pentoxide tube placed in tandem with the first showed no gain in weight; hence the first tube caught all the water-vapour. The remaining nitrogen was driven out by pure dry air before weighing. That water-vapour was actually present was shown by the "melting" of phosphoric pentoxide in the first tube.

Water obtained by Decomposition of Argentic Nitrate.

Experiment number.	Weight of $AgNO_3$ Grms.	Gain in weight of drying tubes. Grm.	Percentage of water found.
25	53	0·0015	0·0028
26	52	0·0011	0·0020
27	44	0·0014	0·0033
Average ..	50	0·0013	0·0027

Thus it is clear that less than 0·003 per cent of water was

held by the argentic nitrate after fusion. There was only one other source from which this mgrm. or so of water might have come, namely, from the copper used for the reduction of the nitrous fumes. Less than 0·0002 grm. of hydrogen retained by 300 grms. of copper, or less than one part in a million, would have been enough to cause this effect; hence it seemed rash to assume that the water did not come from this source. As much hydrogen as this might have come from a trace of moisture in the hundred litres of carbon monoxide used for the reduction of the copper.

The question thus raised was capable of being investigated. For this purpose the mass of copper, reduced just as it would have been for one of the preceding experiments, was twice oxidised by a very large volume of pure ignited air dried with the usual potash towers, and finally with phosphoric pentoxide. This air, having been already passed over red-hot cupric oxide in a hard glass tube and thoroughly dried by pentoxide, could hardly bring with it any water which could be taken up by the following tube of the same material. On one of these occasions, 0·0009 grm. of water was found, and on another 0·0007 grm. Possibly some of this may have come from the atmosphere during the manipulation of the tubes, but a similar amount must be supposed to have been taken during each of the previous determinations. Hence it seems to be permissible to subtract the average 0·0008 grm. from the average result of Experiments 25, 26, and 27, namely, 0·0013 grm. This leaves only 0·0005 grm. as the maximum amount of water held by 50 grms. of carefully fused argentic nitrate, introducing an error of only 1 part in 100,000. As the average of the final series led to a value a trifle over 157·480 grms. as the weight of nitrate obtainable from 100·000 grms. of silver, the correction to be applied for water reduces the result only to 157·479. Possibly not even as much water as this was present in the quantitatively made argentic nitrate, because the relative surface exposed for drying was not so great in the long narrow tube just used as it was in the quartz flask employed for Experiments 10 to 15,

This unimportant change in the synthetic result from 157·480 to 157·479 was the only apparent outcome of these tedious and often exasperating experiments on the decomposition of the nitrate, but in reality more was shown by them. The experience furnished to the experimenters a striking example of the essential importance of taking as much care in determining a small correction as in determining the quantity to be corrected. It, moreover, confirmed the impression that, except in cases like the chloride of zinc, when water acts chemically upon the substance, little or no water is retained by most fused salts. If argentic nitrate, which at 200° is miscible with water in all proportions, sets free so nearly all that it possesses in a current of dry air at this temperature, it is much more likely that other salts, fusing at a higher temperature and possessing a less attraction for water, should be free from it after fusion. This is a reassuring conviction, well worth the trouble spent upon the point.

Attention was now directed to other foreign substances besides water and air which might be present in the synthetic argentic nitrate. Further careful investigation was needed to show that all the silver was combined as nitrate, and that no other impurities were concealed in the salt. The pure pearly whiteness of the cold fused material precluded the possibility of there having been a trace of reduction to metallic silver. The salt was soluble in pure water without residue or turbidity, and maintained its clearness when diluted to half or quarter normal; hence oxide and halogen salts must have been absent. The only other likely impurity seemed to be ammonium salts, nitrite, and excess of nitric acid. Of these possibilities, Stas thought only of the likelihood of the presence of free acid, but each was carefully considered in the present work.

It is known that copper dissolving in nitric acid forms perceptible quantities of ammonic nitrate. Apparently, no similar reaction has been noted with silver, and from an electro-chemical standpoint it seemed unlikely; moreover, ammonic nitrate, if present, would probably be for the most part decomposed by the hour's fusion of the silver salt. Nevertheless, thoroughness demanded evidence on this point. Nessler solution is the most convenient for this test, but silver must first be precipitated from solution in the dark. Light generates chlorine which interferes with the test.

In order to prepare for this search for ammonia, the synthetic nitrate of silver resulting from several experiments was shaken with a slight excess of standard pure sodic chloride until the supernatant liquid was clear; the latter was decanted, made up to 50 cc., and placed in a comparison cylinder. The sodic chloride gave no test with Nessler solution.

The cylinder full of liquid prepared from the argentic nitrate was finally tested by comparison with other cylinders containing known traces of ammonic nitrate mixed with sodic nitrate in concentration equal to that existing in the actual determination. The sodic nitrate had been several times re-crystallised with centrifugal draining, and was shown to be free from ammonia. In this way the following results were attained:—Synthesis 12 was found to contain 0·05 mgrm. of ammonic nitrate, Synthesis 13, 0·06 mgrm., and Synthesis 14, 0·05 mgrm.; in all, 36·5 grms. of argentic nitrate were proved to contain no more than 0·00016 grm. of ammonic nitrate—less than one two-thousandth of 1 per cent. The source of this ammonia was not determined; it might have come from the reduction of nitric acid or from the large volume of air used in evaporating the argentic nitrate. The only possible place where it could have entered with the reagents used in the test was in the sodic chloride solution; this was indeed tested, with negative results, but Nessler's reagent is not very sensitive in the presence of chloride, and a trace of ammonia might have eluded detection. If the amount found had been larger, more time would have been spent upon the matter, and a sample of the argentic nitrate often re-crystallised in an atmosphere free from ammonia would have been used in a blank experiment for comparison; but with such a small trace of impurity this was not worth while.

In summing up the results of the test for ammonia, the amount should be calculated for the quantity of argentic nitrate produced from 100·000 grms. of silver. Thus it is found that 157·480 grms. of fused argentic nitrate could not have contained over 0·0007 grm. of ammonic nitrate.

The next impurity to be studied, nitrous acid, was sought by means of sulphanilic acid and naphthylamine hydrochloride. These were proved with a standard nitrite solution of which 1 litre contained 0·1 grm. of nitrogen. To insure parallel conditions in testing by comparison, pure silver nitrate was prepared with some care. It was thrice re-crystallised from nitric acid with centrifugal treatment, fused in porcelain, then re-crystallised three times more from the purest water in platinum, with centrifugal draining as before. The specimens of fused argentic nitrate resulting from quantitative determinations were dissolved in known amounts of water, and comparison solutions of equal concentration prepared. The crystallised silver nitrate gave no trace of pink colour with the reagents. A fresh solution to which 0·1 cc. of nitrite solution (0·01 mgrm.) had been added gave a pronounced colour, while Determinations 2, 3, and 11 all gave a much fainter barely visible colour; hence it was permissible to conclude that the loss of oxygen from the nitrate on fusion could not have exceeded 0·000005 grm., a wholly negligible quantity.

In seeking for the next impurity, free nitric acid, Stas tested aqueous solutions of his fused silver nitrate with "tournesol," and found them alkaline rather than acid. This alkali may have come from his glass vessels. We used methyl-orange, a more sensitive indicator, and noted that the purest crystallised neutral specimens and the fused salt alike gave equally pronounced acid reactions in solu-

tion. The colour was not modified by the addition of half a mgrm. of nitric acid; therefore the equality in colour does not disprove the presence of free acid in our fused product. Dilute sodic hydroxide freed from carbonate by baric hydroxide threw down a precipitate without changing the pink colour. Hence the indicator was discarded, and the investigation continued with the nephelometer.

The test for acid with the help of this instrument was conducted by adding a very dilute standard caustic alkaline solution to the solution to be tested, and by observing if this addition caused a permanent cloud.

Preliminary trials were necessary, in the first place, in order to determine the conditions best suited for accuracy. It was found that a concentration of nitrate no stronger than 4 grms. in 0·025 litre was best adapted to this work, as argentic hydroxide is distinctly soluble in double this concentration of argentic nitrate. On the other hand, argentic hydroxide precipitated by somewhat concentrated alkali does not quickly re-dissolve in an equivalent quantity of nitric acid, mixed with the dilute argentic solution. It was found that even the precipitate caused by 0·1 millilitre of a two-hundredth normal solution may produce a fairly permanent cloud in spite of the presence of an excess of 0·00003 grm. of nitric acid, enough to dissolve it. Still more dilute solutions behaved much more satisfactorily, however,. A millilitre of a two-thousandth normal caustic solution (equivalent to 0·00003 grm. of nitric acid) added with constant stirring to the pure standard argentic nitrate formed a cloud easily seen in the nephelometer. In case 0·00003 grm. of nitric acid had been introduced before adding alkali, no precipitate was formed under the same conditions. Hence under these circumstances the test attained a degree of sensitiveness suited to the case in hand.

In this way it was found that the argentic nitrate remaining from Synthesis 11 gave a distinct opalescence with the addition of 0·00002 grm. of sodic hydroxide, and an obvious cloud with 0·00003 grm. Hence it was concluded that argentic nitrate fused in a stream of pure air for one hour contains no weighable excess of nitric acid.

The various suspected impurities having thus been duly sought, it is instructive and interesting to tabulate the results. These are as follows:—

	Grms.
Weight of fused $AgNO_3$ from 100,000 grms. Ag	157·480
Correction for weight of—	
Dissolved air	0·000
Retained water	−0·0016
Retained ammonic nitrate	−0·0007
Nitrite	0·000
Free acid	0·000
Corrected weight of argentic nitrate obtainable from 100·000 grms. of pure silver ..	157·478

As the subtractive corrections given in the above table are maximum values, the weight of argentic nitrate in question can hardly be lower than this value, 157·478. On the other hand, it can hardly be higher than the uncorrected value, 157·480. Thus two limits are set, very near together, between which the true value must lie. Obviously, for the present one cannot go very far astray in accepting the mean value, 157,479, and this value will be used in the following discussion.

The Final Result and its Relations to the Values of Atomic Weights of Nitrogen and Silver.

The conclusion reached by the foregoing series of experiments is that 100·000 parts of silver yield very nearly 157·479 parts of argentic nitrate. Among other experimenters, Penny found 157·442; Marignac found 157·424; Stas found 157·474 in one series of seven determinations and 157·486 in another of two; and Hardin found 157·484. From these older figures, by an interesting coincidence Clarke calculated exactly the value found in the present research ("Re-calculation of the Atomic Weights," 1897, p. 64). This coincidence is to be attributed not so much to the efficacy of the method of calculation as to the fact that in this case the impurities in the silver happened to balance exactly the impurities in the argentic nitrate. At first sight it is incomprehensible how Stas, working with slightly impure silver, could have obtained any results higher than the true value; but it must be remembered that his nitrate was fused in a glass vessel, which must have been attacked by the strongly acid nitrate at 220°. Constancy in the weight of the vessel would be no evidence of absence of action, for silver might partly take in the glass the place of the sodium taken from it. Thus a gain in weight due to sodic nitrate might be accompanied with no considerable loss of weight of the vessel. In favour of this hypothesis is the fact that Stas's results steadily decreased in each series as he proceeded with the work; the flask seems to have been less and less susceptible to attack, as is reasonable. If the last two determinations of the first series are taken as the most nearly free from this cause of error, the number 157·466 obtained from them should furnish, by comparison with our number, some clue to the amount of gaseous impurity in Stas's silver. Thus it appears that his silver must have contained nearly 0·01 per cent of impurity—probably more if it is considered that the flask was still not wholly resistant—a conclusion not very different from that reached by Richards and Wells.

Speculations of this kind concerning older work are rather a thankless task, however; there is usually too much that is doubtful to allow them to serve a very valuable purpose. The only object in pursuing the review at all is in order to assure one's self that no real inconsistency exists in the data.

Attention is now directed to a more important matter, namely, the effect of the new experimental result upon the table of atomic weights. This is quickly stated:—The newly advocated low atomic weight of nitrogen is incompatible with the ratio 100·000 : 157·479, if silver is taken as 107·930. If, on the other hand, the new atomic weight of nitrogen is the true one, silver must have a much lower value than this.

The exact figures are given in the following table:—

The Atomic Weight of Nitrogen.

If Ag = 107·930, $AgNO_3$ = 169·967, and N = *14·037*
If Ag = 107·890, $AgNO_3$ = 169·904, and N = *14·014*
If Ag = 107·883, $AgNO_3$ = 169·893, and N = *14·010*
If Ag = 107·880, $AgNO_3$ = 169·888, and N = *14·008*

This series of conditional statements contains in a nutshell the result of the present investigation. In order to decide between the alternatives, other compounds must be further studied, especially the chlorates and the ammonium salts. Investigations in both of these directions have already been begun in the Chemical Laboratory of Harvard College.

Summary.

Argentic nitrate was made from pure silver, and the gain in weight was carefully noted.

In the course of the work, a new and convenient apparatus for quantitative evaporation was devised. Quartz flasks were used as a part of it.

The argentic nitrate was fused until constant in weight; it was carefully tested for dissolved air, retained water and ammonia, and nitric and nitrous acids. Only the second and third of these impurities could be detected by tests proved to be adequate, and these only in mere traces, between 0·001 and 0·002 per cent in all.

The outcome was that 100·000 parts of pure silver produced 157·479 parts of argentic nitrate. If, then, silver is taken as 107·93, nitrogen must be 14·037; or if silver is taken as 107·880, nitrogen must be 14·008, oxygen being 16·000.

ON THE ESTERIFICATION OF SUCCINIC ACID.

By I. K. PHELPS and J. L. HUBBARD.

In a former paper from the Kent Chemical Laboratory of Yale University (*Am. Journ. Sci.*, xxiii., p. 211) it has been shown that succinic acid analytically pure may be prepared from succinic ester by hydrolysis in presence of a small amount of nitric acid; and, further, that the acid prepared in this way is of a decidedly higher degree of purity than that of the so-called chemically pure acid of commerce. This paper concerns the study of certain conditions under which the preparation of the pure diethyl ester, $C_2H_4(COOC_2H_5)_2$, is readily made, and also certain conditions under which the esterification of the acid seems to be almost quantitatively complete.

The reaction for the formation of an ester from an alcohol and an acid with the elimination of water is a common example of what is termed a reversible reaction. In order to avoid reversion of the reaction, various methods of dehydration have been made use of in the processes brought out for the formation of esters. This seems to have been accomplished most successfully by Fischer and Speier (*Ber.*, 1895, xxviii., 3252), although as early as 1864 Carey Lea (*Am. Journ. Sci.* [2], xxxix., 210) showed that in the esterification of oxalic acid there is an advantage in acting upon the acid in a tube with gaseous alcohol, in comparison with the usual method of esterification by heating oxalic acid with alcohol. Fischer and Speier have shown that when 1 part by weight of acid and 3, 4, or 5 parts of absolute alcohol containing 1 or 3 per cent of hydrochloric acid are boiled on a return condenser for four hours, the product poured into cold water after distilling off half to three-quarters of the excess of alcohol, the aqueous mixture shaken out with ether, the ethereal extract dried and fractioned, gives of the ester a yield which is considered good when compared with the amount obtainable by other methods. While this procedure generally gives good yields when used for the esterification of organic acids, the esterification of each individual acid must, nevertheless, be studied by itself in detail; for, as Fischer has stated, the best yields in given cases are obtained by varying the general procedure.

In Fischer's procedure for the preparation of the ethyl ester of succinic acid the absolute alcohol is a solvent for succinic acid and its esters. It is, also, a dehydrating agent. But inasmuch as the water remains with the alcohol and the esters, it may still be active in holding back the completion of the reaction in which the normal ester is formed. Fischer's best yield was 73·9 per cent of that theoretically possible.

In the work here described the attempt has been made to reduce the proportion of water, the presence of which may retard the completion of the action, by introducing the vapour of alcohol charged with dry hydrochloric acid into the solution of succinic acid in alcohol also charged with hydrochloric acid, and allowing the alcohol, water, and hydrochloric acid to pass out from the hot solution to a condenser.

In every experiment recorded in the table, alcohol charged with dry hydrochloric acid was boiled in a 500 cc. flask fitted with a separating funnel and an outlet tube, and passed in vapour to the bottom of a 250 cc. sideneck flask containing a definite weight of succinic acid and a definite volume of alcohol charged with a definite weight of dry hydrochloric acid. The temperature of the mixture in the sideneck flask was kept between 100° and 110° by heating the flask in a bath of sulphuric acid and potassium sulphate, and this temperature was indicated by a thermometer dipping in the mixture and held in a two-bored stopper fitted to the sideneck flask and carrying also the glass tube for the introduction of the vapour (H. Scudder, *Journ. Am. Chem. Soc.*, 1903, xxv., 161). The vapour liberated in the sideneck flask passed through the sideneck to a condenser and was collected as the liquid distillate. This distillate contained whatever ester may have passed along with the hydrochloric acid, alcohol, and water mixture. As succinic ester boils at 213·3° and as the temperature in the sideneck flask was maintained between 100° and 110°, the amount of succinic ester in the distillate was necessarily a small part of the total ester produced in the reaction.

The mass of ester with its impurities from the sideneck flask was poured into a separating funnel containing a little ice, the last traces of the liquid being transferred from the flask to the funnel by successive rinsings with ether. The impure ester in the funnel was treated with an excess of dissolved sodium carbonate, and the water solution was drained off from the supernatant mixture. This mixture was washed free from sodium carbonate with a water solution of sodium chloride of sufficient density to separate it easily from the mixture. To recover any portion of the ester carried along in the water solution of sodium carbonate and the wash-water containing sodium chloride, each solution was shaken out separately three times with fresh portions of ether which were added to the main portion of the mixture. These mixtures of ester in the ethereal solutions were gathered in a 250 cc. sideneck flask connected with a 100 cc. sideneck flask as a receiver in the usual way for a vacuum distillation. The lower boiling-point impurities in the succinic ester, presumably composed chiefly of ether, alcohol, and water, were removed by allowing a gentle current of air to pass through the apparatus while the flask containing the ester solution was heated in a water-bath raised finally to 60° until the pressure registered on the manometer (15 mm.) indicated that only succinic ester remained in the flask to be distilled. The ester was then distilled over by heating the 250 cc. flask in a bath of sulphuric acid and potassium sulphate at 140—150°, and collected in the second flask, which was cooled by allowing a current of cold water to strike it constantly during distillation. The last traces of ester left on the distilling flask were removed by flaming suitably the sidewalls of the flask and at the same time increasing the current of air that was passing through the apparatus. The increase in weight of the receiver gave the weight of the succinic ester left in the sideneck flask when the acid was esterified as completely as possible under the conditions imposed in each experiment.

To recover whatever succinic ester might have been carried to the condenser with the alcohol and other vapours during esterification, the acid alcoholic distillate was chilled with ice, diluted with three or four times its volume of water, and shaken out three times in a separating funnel with fresh portions of ether. The ethereal solution thus obtained was treated with an excess of sodium carbonate in solution, washed with distilled water, and distilled *in vacuo*, in the manner described above, to separate the low boiling-point materials present, largely ether, alcohol, and water, and finally to distil the succinic ester, which was weighed.

The sources of loss inherent in this method for the preparation of pure succinic ester were carefully studied. It was found, first, that if a known weight of pure succinic ester, 75 grms., was taken in a separating funnel, shaken with sodium carbonate solution containing ice, separated from the sodium carbonate solution, washed with distilled water containing common salt, and united with the portions of ester carried on mechanically, and recovered from the water solutions by shaking out three times with fresh portions of ether, that the weight of the ester recovered on distilling *in vacuo* the ethereal solution containing some water was less than the amount taken by only 0·60 grm.

It was found, further, that when a portion of 5 grms. of succinic ester was put with 300 cc. of the alcoholic hydrochloric acid mixture used in esterification and treated exactly in the manner described for the recovery of the ester from the acid alcoholic distillate, the mass of succinic ester recovered showed a loss of only 0·50 grm.

It was found, also, that when 75 grms. of succinic ester held in a flask fitted with a receiver and capillary tube for a vacuum distillation were heated for an hour in a water-

No.	Succinic acid.	Alcohol with HCl.		Succinic ester.				Reaction time.	
				Theory.	Found.	Found in distillate.	Total yield.		
	Grms.	Cc.	Per cent.	Grms.	Grms.	Grms.	Per cent.	Hours.	Minutes.
				A.					
1.	50	100	1·25	73·7	50·07	0·60	68·0	0	30
2.	50	100	1·25	73·7	55·06	0·00	74·9	1	25
3.	50	150	1·25	73·7	62·26	0·47	85·1	0	45
4.	50	200	1·25	73·7	66·30	0·90	91·2	1	55
5.	50	200	1·25	73·7	66·27	1·40	91·8	1	50
6.	50	250	1·25	73·7	65·60	2·15	91·9	2	25
7.	50	250	1·25	73·7	69·05	1·65	95·9	3	0
8.	50	300	1·25	73·7	67·10	3·25	95·5	4	0
9.	50	300	1·25	73·7	69·85	1·65	97·0	5	20
10.	50	350	1·25	73·7	63·80	4·70	92·9	2	15
11.	50	350	1·25	73·7	67·31	2·65	94·9	5	0
				B.					
12.	50	200	1·25	73·7	66·26	1·82	92·9	2	20
13.	50	200	1·25	73·7	65·30	5·27	95·8	3	0
14.	50	350	1·25	73·7	66·05	2·90	93·6	3	45
15.	50	350	1·25	73·7	68·75	1·57	95·4	4	30
16.	50	200	10	73·7	59·10	5·43	87·4	0	20
17.	50	200	10	73·7	67·90	1·50	94·2	2	25
18.	50	200	10 (*a*)	73·7	68·32	3·30	95·8	1	45
				C.					
19.	50	200	1·25					2	10
		150	10	73·7	67·60	1·80	94·2	1	0
20.	100	300	1·25					2	0
		200	10	147·4	132·80	6·32	94·4	1	15
21.	50	200	1·25					1	25
		100	10	73·7	69·50	2·50	97·7	1	0
22.	100	300	1·25					2	0
		200	1·25	147·4	135·25	4·81	97·5	1	0

(*a*) And gaseous.

bath at 60° under a pressure of 15 mm., that the weight of the ester was diminished by less than 0·05 grm.

From these experiments it appears that the losses in the preparation of pure succinic ester should not exceed 2 grms.

While the general process of treatment described above was applied in all the experiments recorded in the table, some experiments differed from others in respect to the proportions of the reagents and to supplementary treatment.

In the experiments of Series A of the table the alcohol used was 99·5 per cent pure, and this was charged with dry gaseous hydrochloric acid to the amount of 10 grms. to the litre. The succinic acid was the pure acid of commerce.

In the experiments of Series B, the alcohol used was made more nearly absolute than that used in Series A by heating 99·5 per cent alcohol for an hour over fresh calcium oxide with a return condenser, and distilling to a protected receiver open to the air through a calcium oxide tube. In Experiments 12, 13, 14, and 15 succinic acid prepared pure by hydrolysis of the ester in the presence of nitric acid was used, in the others the acid of commerce. The alcohol was charged with dry hydrochloric acid to the amount of 10 grms. to the litre. In 16 and 17 the alcohol was charged with dry hydrochloric acid to the amount of 80 grms. to the litre, and in Experiment 18 the alcohol originally charged with 80 grms. to the litre was reinforced by passing into the sideneck flask a rapid current of hydrochloric acid gas, dried by passing through concentrated sulphuric acid in a bead tower of 30 centimetres length, simultaneously with the charged alcohol vapour.

An inspection of the yields obtained in the experiments of Series B, in which the more nearly absolute alcohol was employed with experiments otherwise nearly similar of Series A in which alcohol of 99·5 per cent purity was used, show perhaps a trifling advantage in favour of the slightly stronger alcohol. Thus, 12 of B gave 1 per cent more yield than 6 of A, though in the latter 25 per cent more of the charged alcohol was used under conditions otherwise closely similar; 13 of B gave about the same yield as 7 of A, though in the latter 25 per cent more of the charged alcohol was used; but the yield in 15 of B with an increase of 16·6 per cent in the amount of charged alcohol and 12·5 per cent in the reaction time was a trifle less than that of 8 of Series A.

Upon examining the yields of experiments in which equal amounts of the alcohol similarly charged were brought into action with a given amount of succinic acid, it appears, as is natural, that the amount of succinic ester produced increased with the time of reaction. This inference becomes evident in a comparison of Experiments 1 and 2, 6 and 7, 8 and 9, 10 and 11, 12 and 13, and 14 and 15.

It appears also that the proportion of similarly charged alcohol, for a given weight of succinic acid, affects the yield of ester—very markedly at first, but that the effect of increasing beyond a moderate limit the amount of alcohol passed through the apparatus in a given time is not so important. This effect is not surprising when it is remembered that the larger part of the water liberated is found early in the reaction, and that the effect of the continued distillation would be naturally more in evidence at that time. Thus the yield of Experiment 3, in which 150 cc. of the charged alcohol were used, is 8 per cent greater in half the reaction time than that of Experiment 1, in which 100 cc. of the same mixture were employed; while the difference between the yield of 6 from 250 cc. of the charged alcohol and that of 10 from 350 cc. of the similarly charged alcohol is 1·1 per cent. In 12 of B with purer acid and alcohol of greater concentration the process gives the same yield as in 10.

Increase in the amount of dry hydrochloric acid with which the alcohol is charged is effective in increasing the yield. From 18 it appears that a current of dry hydrochloric acid has such an effect. This appears when 18 is compared with 17, and more strikingly when compared

with 5, where the differences are largely the concentration of the hydrochloric acid with a gain of 4 per cent in the yield of 18.

In the experiments of Series C the process of forming the ester was conducted in two stages in an attempt to cause the esterification of the final portions of the succinic acid more advantageously. It is obvious from the work recorded in Series A and Series B that it is comparatively easy to cause the esterification of a little more than 90 per cent of the acid. In Experiment 19, after the first portion of alcohol—200 cc.—of highest purity charged with dry gaseous hydrochloric acid in the proportion of 10 grms. to the litre had acted upon the commercial succinic acid in the manner described above, a fresh portion of alcohol, 150 cc., containing 10 per cent of dry hydrochloric acid gas was put with the ester solution, and the whole was heated at the boiling-point for an hour with a return condenser in an attempt to learn whether a fresh mass of the absolute alcohol hydrochloric acid mixture containing 10 per cent of hydrochloric acid could serve sufficiently as a dehydrating agent to allow the completion of the reaction. It does not seem evident that the second treatment is markedly advantageous in completing the reaction. Its effect, if anything, is slight. In case of Experiment 20, after completing esterification of the pure acid so far as possible with 200 cc. of the purest alcohol with hydrochloric acid in the usual way, 200 cc. more of the same alcohol with 10 per cent of hydrochloric acid was driven through the ester as in the first half of the procedure. The effect of this second treatment is not apparently of marked advantage in esterifying the final portions of the acid. In Experiments 21 and 22 after the treatment for esterification, as given earlier, was completed, all low boiling-point material, chiefly alcohol, water, and hydrochloric acid, was removed from the ester in the sideneck flask by a vacuum fractionation, carried out by heating the flask in a water-bath finally at 60° with the pressure on the manometer registering 15 mm., this pressure and temperature being maintained fifteen minutes. The material in the flask was then treated with fresh alcohol and hydrochloric acid in amounts given in the table in gaseous form as in the first half of the experiment. Pure succinic acid was used in case of 21, and commercial acid in case of 22. This process of removing traces of water by the intermediate vacuum distillation from the mixture containing the ester is obviously very effective, and the yield of Experiment 21 is the best of the entire suite. Indeed, if it be recalled that the losses inherent in the processes of obtaining the pure ester are a fraction more than a grm., it is seen that all of the acid taken appears as ester except a portion as small as 0·30 of a grm.

So it appears that while high purity of the succinic acid and the alcohol, the proportion of the hydrochloric acid, the time of the reaction, are all influential factors in the process of forming the ethyl ester, the thing most important in obtaining a high yield is the removal of the water as it is formed in the reaction; and we have found that this may be done most easily and very effectively by passing the vapour of alcohol charged with a small proportion of hydrochloric acid into a continuously distilling mixture of succinic acid and alcohol also charged with hydrochloric acid. By thus acting with a total volume of 300 cc. of the alcohol charged with 1·25 per cent of hydrochloric acid upon 50 grms. of succinic acid, the yield in action of five hours reached 97 per cent of the theory, while this time of action was cut in two, and the yield at the same time slightly increased to 97·7 per cent by interpolating in the process a vacuum distillation to remove water more effectively from the reacting mixture.

Even if the usually small amounts of ester which pass to the distillate are disregarded in the process of recovery, the yield of the process in its simpler form is still 20 per cent higher than that of any other described procedure known to us for making the ethyl ester of succinic acid by the interaction of the acid and alcohol.—*American Journal of Science*, xxiii., p. 368.

NOTICES OF BOOKS.

The Medico-Physical Works of John Mayow, LL.D., M.D. Edinburgh: The Alembic Club; James Thin. London: Simpkin and Co. 1907.

The Alembic Club has already won the gratitude of students of historical chemistry, who find their reprints of the classics of the science of great value and interest, and this seventeenth volume of the series will be particularly welcome, for it contains the works of Mayow, which have hitherto been almost inaccessible to English readers. The translation has been performed literally from the edition of 1674, printed at Oxford, and in order that the reader's survey of Mayow's views may be as far-reaching and correct in detail as possible the whole of his scientific works are included. The five treatises show that he was far in advance of his time as regards his ideas about chemical phenomena, more especially on the nature of combustion, and he showed considerable skill in devising and adapting experimental methods, the quaint illustrations of his apparatus which are reproduced revealing his great ingenuity. The papers are not provided with explanatory notes or comments, which indeed they do not require, for Mayow's language was very clear, and it is easy to grasp his meaning and follow his argument, even when he uses unfamiliar phrases or words to describe the phenomena he observed. His physiological work was almost on a level as regards importance with his chemical discoveries, and the advances due to him in the two branches together give him a strong claim to be regarded as one of the most eminent of English men of science.

The Physiology of Alimentation. By Dr. Martin H. Fischer. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1907.

This book gives an account of the physiology of alimentation, more especially from a medical point of view. It opens with a lengthy discussion of the mechanical phenomena of alimentation, which is excellently illustrated by reproductions of X-ray photographs, sent to the author by Dr. Cannon. Then the chemical constituents of the juices which act upon the food are considered, and much attention is paid to the subject of ferments and fermentation. This part of the book appears to be well up to date, and some specially interesting or important subjects, as, for example, Weinland's work upon antiproteinase, are discussed fully; the bacteriology of the alimentary tract is also well treated. The later part of the book deals with the alimentary tract as an absorptive and as an excretory system, and here the author appears to have committed an error of judgment in assuming that his readers would require an exposition of the elementary laws of osmosis. However, the whole book, while not aspiring to be an important original contribution to physiological literature, or even a complete text-book on the subject of alimentation, bears evidences of careful, well-planned work, and the subject is handled in a particularly interesting manner.

Water Analysis. By J. Alfred Wanklyn, M.R.C.S. Eleventh Edition, revised by W. J. Cooper. London: Kegan Paul, Trench, Trübner, and Co., Ltd. 1907.

The late Professor Wanklyn's experience of the analysis of water was extensive, and his text-book on the subject has long been regarded as an important authority. The eleventh edition is a reprint of the tenth, giving detailed descriptions of methods of carrying out analyses, both for general sanitary and special purposes, together with useful notes on the usual methods of drawing up reports and the conclusions to be drawn from the results of experimental work. The book contains in addition a short biographical memoir of Prof. Wanklyn, in which an account is given of his work upon various chemical subjects, some of which was of considerable importance.

The Evolution of Matter, Life, and Mind. By W. STEWART DUNCAN. Philadelphia: Index Publishing Company. 1907.

THE Preface to this book arouses in the reader hopes which a very short examination of the text shows are not destined to be realised. An exposition of monistic philosophy as applied to psychical science should be interesting, and a well-balanced criticism of the theory of psycho-physical phenomena would be welcomed by the many who feel that the time is ripe for a great advance of our knowledge of this subject. But the book falls far short of the standard which a guide to modern thought should reach, and the writer does not exhibit that tolerance and moderation without which any book upon a polemical subject is almost worthless. He wastes much space in proving what the majority of his readers will regard as already firmly established, and lays undue stress upon such of his own prophecies as appear to be justified by facts, while at the same time losing no opportunity of criticising those who do not agree with him or who paid scant attention to his theories. The reader will therefore be not unprepared to find that some of the most sweeping statements are at any rate open to question in the form in which they are put forward, and when he reads that to call a chemical compound by its name, even if it possibly appears unwieldy to the uninitiated, is mere bluffing and fooling, as if chemical names, such as paraoxyphenetol, were a purely empirical means of identifying substances, used as blinds to conceal their real nature, he will not be surprised at anything that comes later. The author has evidently still to learn what the term "organic" means when applied to a chemical compound.

Organic Chemistry for Advanced Students. By JULIUS B. COHEN, Ph.D., B.Sc. London: Edward Arnold. 1907. Pp. 632.

IN his Preface the author informs us that this book is not in any way to be looked upon as a book of reference. It has been prepared from notes of a series of lectures delivered to advanced students, and therefore assumes that the reader is already well acquainted with the principles of organic chemistry.

It would be impossible, even in a book of this size, to deal adequately with all the various developments of so large a subject; and as the tendency now-a-days is to specialise in every subject, so, in this volume, has the author specialised on a certain number of sub-divisions of organic chemistry.

The book is divided into fourteen chapters, beginning with an historical introduction. In Chapter II. he deals with isomerism and stereoisomerism, followed by chapters on the stereochemistry of unsaturated and cyclic compounds and the stereochemistry of nitrogen. Chapters V., VI., and VII. are devoted respectively to isomeric change, steric hindrance, and condensation. Up to this point the author has dealt principally with theories, typical reactions, and changes, but in Chapter VIII. we come to the carbohydrates, which are among the principal products of plant life, and include the important group of the saccharoses.

Fermentation and enzyme action are the subjects of Chapter IX., followed by the purine group, which comprises uric acid and the xanthine bases, in the succeeding chapter.

Chapter XI., on the proteins, embraces a large and ill-defined group of substances derived directly or indirectly from living matter; they form the chief constituents of the protoplasm of the majority of cells and enter into the composition of animal tissues and secretions; they are classified on pages 412—415.

The benzene theory next engages our attention, commencing with Kekulé's benzene formula, followed—some pages further on—by Kekulé's dynamic hypothesis and the dynamic formula for benzene.

Chapter XIII. is on the terpenes and camphors—an important group, comprising natural and artificial perfumes.

The alkaloids form the subject of Chapter XIV. and last. These consist of numerous oily and crystalline basic substances obtained from certain plants, and are characterised by very marked physiological properties, making them of special interest both to the chemist and physiologist. The history of the successive stages in the synthesis of these bodies is the main object of this chapter.

The book is one of considerable interest, and though not compiled on the lines of an orthodox text-book, we feel sure that it will be well received by those who are going beyond the ordinary college course of organic chemistry. It is well printed in large clear type and provided with two excellent indices, one of "subjects" the other of "authors."

CORRESPONDENCE.

RELATION BETWEEN THE ATOMIC WEIGHTS OF THE ELEMENTS.

To the Editor of the Chemical News.

SIR,—If we consider a table showing Mendeleeff's classification of the elements, it will be found that the members of each group are very nearly made up of ascending multiples of the top member of each group added to a regular multiple of the number 16. To illustrate, I give Group I. of Mendeleeff's classification:—

New series.			Difference.
0.		Li = 7·03	
1.	16 + 7·03 = 23·03	Na = 23·05	0·02
2.	2 (16) + 7·03 = 39·03	K = 39·1	0·07
3.	3 (16) + 2 (7·03) = 62·06	Cu = 63·6	1·54
4.	4 (16) + 3 (7·03) = 85·09	Rb = 85·4	0·31
5.	5 (16) + 4 (7·03) = 108·12	Ag = 107·9	0·22
6.	6 (16) + 5 (7·03) = 131·15	Cs = 132·9	1·75
7.	7 6	—	
8.	8 7	—	
9.	9 (16) + 8 (7·03) = 200·24	Au = 197·2	3·04

We may express the above relation in an empirical formula, thus—

$$mx + (m \pm n)y = W;$$

where m = number of series (He series = 0), x = 16, y = the top member of the group, and n = a positive or negative integer between 0 and 5.

A table can be arranged so that n has a regular + value in the F, Fe, Co, Ni groups and a − value in all the others. To illustrate this, and also the effect of giving y a slightly different value in some cases, I give the Be group:—

Series.			Difference.
0.	y = 8	Be = 9·1	1·1
1.	16 + 8 = 24	Mg = 24·1	0·1
2.	2 (16) + 8 = 40	Ca = 40·1	0·1
3.	3 (16) + 2 (8) = 64	Zn = 65·4	1·4
4.	4 (16) + 3 (8) = 88	Sr = 87·6	0·4
5.	5 (16) + 4 (8) = 112	Cd = 112·4	0·4
6.	6 (16) + 5 (8) = 136	Ba = 137·4	1·4
7.	7 6		
8.	8 *6	*n = 2	
9.	9 (16) + 7 (8) = 200	Hg = 200	0
10.	10 (16) + 8 (8) = 224	Rd = 224	0

Except in the Li group, n changes in value at the 4th or the 8th series in each group.

Might not this relation be used to explain Sir William Ramsay's recent discoveries concerning the disruption of different elemental atoms by the Rd emanation? Accepting for the moment the supposition that the atoms are made up of groups, as indicated above, and that group 16 is a

strong base or radicle, and also that the atomic weight of the α-particle is 2, then upon bubbling the emanation through water we might get the following reaction:—

$$H_2O^* + 2\ \alpha\text{-particles} = (16+4) + H_2 = \dagger Ne + H_2$$

* O=16. † Ne=(16+4)=20.

Or taking another case (see Li group above)—

$$\{3\ (16) + 2\ (7)\} + 2\ \alpha\text{-particles} = \{2\ (16)+4\} + (16+7)+7;$$

in other words,—

$$Cu + 2\ \alpha\text{-particles} = Ar + Na + Li.$$

I would very much like to know whether these relations have ever been pointed out before, and, if so, where I can find an account and explanation of it.—I am, &c.,

W. Denham Verschoyle.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlv., No. 12, September 16, 1907.

Method of Rapidly Determining Carbon and Hydrogen in Organic Substances.—Pierre Breteau and Henri Leroux.—The combustion tube consists of an outer nickel tube into which an inner porcelain or quartz tube is fixed. The latter has rolled round it a platinum spiral, which can be raised to a dull red heat by means of an electric current. The substance to be burnt is placed in a porcelain boat, and is introduced into the combustion tube in a glass tube to which a semi-capillary tube is fused. The glass tube is placed so that one or two turns of the platinum spiral are within the wide part. A current of dry oxygen enters the glass tube by the semi-capillary, and another circulates round the outside of the glass tube. The further end of the nickel tube is connected with the absorption apparatus. When the platinum spiral is dull red the substance is very gently heated. The combustion is proceeding satisfactorily when a small flame is seen playing round the end of the spiral. When the substance has been decomposed the residual carbon is heated strongly, the rate of the inner current of oxygen being greatly increased. A combustion takes from fifteen to forty minutes, according to the nature of the organic substance.

No. 13, September 23, 1907.

Methylation of Ethyl Alcohol from the Point of View of the Tendency of the Haloid Ethers to Isomerise.—Louis Henry.—It is a remarkable fact that the alcohols and their acetic ethers are structurally stable, while the haloid ethers readily isomerise. This isomerisation leads to the fixation of the halogen atom in a carbon chain containing less hydrogen, and even in the least hydrogenated chain. Sometimes the carbon nucleus itself remains intact, and sometimes it undergoes a deep-seated change in its structure, thus:—

$CH_3—CH_2—CH_2X$ isomerises to $CH_3—CHX—CH_3$

$H_3C>CH—CH_2X$ „ „ $CH_3>CX—CH_3$

H_3C, $H_3C>C—CH_2X$ „ „ $H_3C>CX—CH_2—CH_3$.

These isomeric transpositions are effected with different degrees of facility. When the different groups of haloid ethers corresponding to the alcohols $C_nH_{2n+1}OH$, which can be attached by methylation (*i.e.*, replacement of hydrogen fixed to carbon by $—CH_3$) to the simplest of the polycarbon alcohols (ethyl alcohol. C_2H_5OH), are considered, the general conclusion drawn is that the isomerisation of the haloid ethers is effected most easily when there is least hydrogen in the neighbourhood of the ether haloid chain or in the chain itself. The trimethyl haloid ethers, $(CH_3)_3\equiv C—$, are particularly remarkable in this respect. This is another instance of the stability which the presence of much hydrogen gives to polycarbon nuclei.

Various Cast Irons.—Léon Guillet.—The author has already shown that silicon and aluminium favour the formation of graphite, while the presence of chromium tends to prevent it. Nickel resembles silicon and aluminium in this respect, and thus the general conclusion to be drawn from these researches is that elements which can dissolve in iron lead to the formation of graphite, while elements which form a double carbide with cementite (manganese and chromium) hinder it.

MEETINGS FOR THE WEEK.

Thursday, 24th.—Chemical, 8.30. "Constitution of Phenol- and Quinol-phthalein Salts—a Contribution to the Quinonoid Theory of Colour," by A. G. Green and P. E. King. "Poly-ketides," by J. N. Collie. "Production of Orcinol Compounds by the Action of Heat on the Sodium Salt of Ethylacetoacetate," by J. N. Collie and E. R. Chrystall. "Simple Gas Generator for Analytical Operations, by J. M. Sanders. "Some Double Ferrocyanides of Calcium, Potassium, and Ammonium," by J. Campbell Brown. "Halogen Determination in Organic Substances," by J. Moir. "Racemisation by Alkali as applied to the Resolution of *r*-Mandelic Acid into its Optically Active Isomerides," by A. McKenzie and H. A. Müller. "Optical Activity of Cyclic Ammonium Compounds," by F. Buckney and H. O. Jones. "Keten, a New Anhydride of Acetic Acid," by N. T. M. Wilsmore. "Action of Phosphorus Pentachloride on Hydroxytrimethyl-succinic Ester, 1.2-Dimethyltrimethylene-1.2-dicarboxylic Acid," by H. Henstock and B. E. Woolley.

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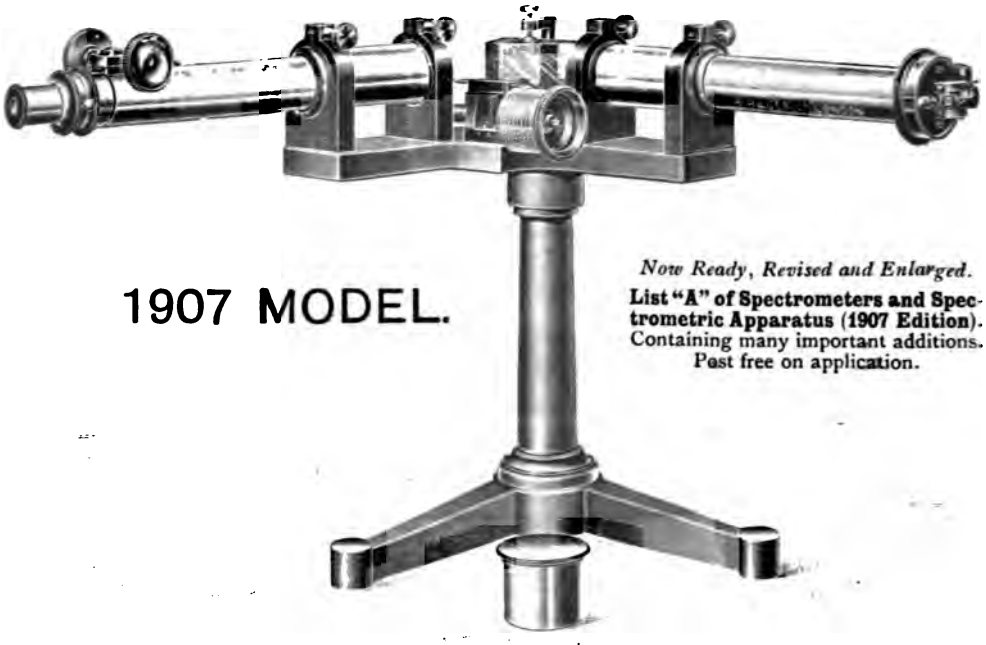

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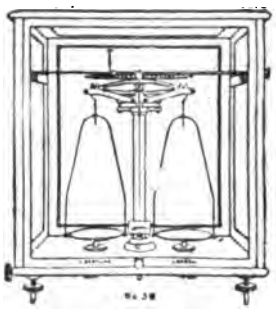

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THE FRUIT OF THE *CELESTRUS SCANDENS* AND *SOLANUM DULCARUM*.

By A. A. WELLS and GRANT S. REEDER.

THE fruit of the *Celestrus scandens*, climbing bitter-sweet, was gathered in some low waste places near Mount Vernon in Eastern Iowa in the autumn of 1904. It was kept at the air temperature until January, 1907, when work upon it was begun.

The berry thus dried when separated from the pod weighed about 0·152 grm. After igniting thoroughly in a platinum crucible the ash was found to weigh 0·005 grm.

The seeds can easily be separated from the pulp by gently squeezing the berry in the hand. Each berry contains from four to six seeds, which are similar in size and colour to raisin seeds. The berries contain such a large amount of sugar that in the air they do not lose more moisture nor become drier and harder than the raisin as it is ordinarily found. The pulp surrounds the seeds in a relatively thin layer, representing not more than one-quarter of the entire bulk of the berry.

The pod which encloses the berry is composed of three sections; these open as the fruit ripens. The inside of the pod is of a light orange colour, the outside of a much darker shade. The fruit grows in clusters, somewhat suggesting clusters of grapes.

There were on hand for the analysis about six and a-half quarts of berries, with the pods. The berries were separated from the pods by hand, which proved to be a slow process, and there were found to be three pints. These were transferred to a flask, covered with distilled water, and kept at nearly the boiling temperature for forty-eight hours. The liquid was then drained off, and the berries set aside for further work upon them.

The water extract gave a satisfactory test for sugar with Fehling's solution, and to determine the kind a portion of the liquid was evaporated nearly to dryness on the water-bath. As the drying continued no amount of stirring would give a crystalline mass, although it became hard enough to break into chunks. Upon standing in the air for some time the mass was deliquescent and appeared like a thick syrup.

The sugar was treated with phenylhydrazine in varying proportions, but the most satisfactory results were obtained by taking 0·1 grm. sugar, 0·2 grm. phenylhydrazine hydrochloride, and 0·3 grm. sodium acetate. The mixture was placed in a test-tube with 10 cc. distilled water. This was loosely corked and kept in a bath of boiling water. After two minutes a precipitate resulted, indicating that the sugar is fructose. The experiment was repeated several times, the results pointing in the same direction.

The remaining portion of the water extract was further tested; the solution gave a distinct acid reaction with litmus, showing the presence of a free acid or an acid salt. Upon the addition of calcium chloride to an alkaline solution, a precipitate soluble in acetic acid resulted, indicating the presence of a tartrate. Ferric chloride was added to another portion, and the resulting black colour indicated either tannic or gallic acid. Upon the addition of a little potassium cyanide a red colour was obtained, showing that it is gallic acid. Lead acetate was next added, when an orange-coloured precipitate, soluble in acetic acid, resulted. This is a test for the colouring matter fisetin. To verify this, we added a solution of stannous chloride and obtained the characteristic orange precipitate.

The ash of the berries effervesces in hydrochloric acid. The carbonate doubtless results from the decomposition of an oxalate.

The seeds were separated from the pulp by placing the berries in water and rubbing them between the hands. The loosened pulp was removed by running water, in the manner of "panning" ore. The seeds were dried and treated in a flask, to which was attached a perpendicular condenser, with successive portions of boiling alcohol, for forty-eight hours.

The alcoholic solution was poured off, and upon the addition of water it became turbid and had the odour and colour of sweetened chocolate in milk. This was distilled with steam and the distillation continued for a number of hours. The distillate had a pleasant nut-like odour, which disappeared on exposure to the air; no trace of oil other than this odour was observable in the distillate. During the process of distillation a resinous substance collected around the flask and appeared as a scum on the liquid. On cooling the contents of the flask nearly to zero, the substance became solid and was easily separated. By treating this with warm alcohol a portion dissolved, and, upon filtering, the insoluble residue was found to be a dry, tasteless, and odourless substance of a chocolate appearance. On adding water to a small portion of the filtrate in a test-tube, the turbidity reappeared as before the distillation with steam.

The alcohol was removed by distillation, and a yellow oil remained, with an odour similar to that which went over in the distillation with steam. An alcoholic solution was treated with bone-black and further purified by treating alternately with alcohol and ether. It crystallised in needles which melted at 62°; it is therefore palmitic acid.

After drying the seeds that had been treated with alcohol, they were crushed in a mortar, placed in a flask connected with an inverted condenser, and treated for several hours on a warm water-bath with successive portions of ether. Two oils were extracted by this process, one of which is soluble and the other insoluble in alcohol. The two oils could be separated by treating several times with alcohol in a separating funnel, the alcoholic solution rising to the top. The soluble oil was lemon-yellow in colour, the insoluble one was orange. We were unable to crystallise either oil.

The soluble oil was first saponified by treating it with an alcoholic solution of caustic potash. Afterwards, by treating it a number of times with ether, a solid was obtained which melted at 16°; this indicated olein with a slight admixture of palmitin. The other oil, when saponified and purified with ether in the same way, gave a solid with a higher melting-point, but not sufficiently high for palmitin. As a small quantity of palmitic acid was obtained from the alcoholic extraction, it seemed reasonable to infer that this oil also was a mixture of olein and palmitin, in which the palmitin predominated.

The pods were treated in the same manner as the pulp of the berries, and were found to contain the same substances.

The Solanum dulcamara.

The *Solanum dulcamara* (deadly nightshade) berries were gathered August 20, 1906, at Sylvan Beach, New York, where they grow in rich profusion. They greatly add to the charm of the river banks of that wild and interesting region. Thoreau writes regarding them:—"The berries are another kind which grow in drooping clusters. I do not know any clusters more graceful and beautiful than these drooping cymes of scented or translucent cherry-coloured elliptical berries. They hang more gracefully over the river's brim than any pendant in a lady's ear. Yet they are considered poisonous, not to look at, surely. But why should they not be poisonous? Would it not be bad taste to eat these berries, which are ready to feed another sense?"

About 100 grms. of the berries, which had been thoroughly dried and pulverised in a meat grinder, were placed in a 500 cc. flask fitted with a perpendicular con-

denser. These were treated with ten successive portions of hot alcohol, making use of the water-bath. The alcoholic extract was deeply coloured red. The alcohol was removed by distillation, and there remained a thick sticky substance, brown in colour, with an odour similar to molasses. The substance was easily shown to contain sugar by its reduction of Fehling's solution. The treatment with alcohol did not remove all the colour from the fruit. Several portions of hot water were afterwards added, which extracted all the red colour. The water extract was found to contain sugar.

A portion of the liquid extract was heated in a beaker glass, and ammonia and calcium chloride were added. A small precipitate soon appeared. This was filtered cold to allow the citrate, if any were present, to pass through. The precipitate dissolved in acetic acid, indicating tartaric acid. The tartaric test was confirmed by diluting a portion of the liquid extract largely with water, adding 2 cc. of acetic acid, a few drops of a solution of potassium acetate, 15 grms. of finely powdered potassium chloride, and 20 cc. of alcohol. After standing about twenty hours quite a heavy precipitate appeared.

Two grms. of the berries were placed in a platinum crucible. These were gently heated at first, and the heat was gradually increased. There was noticed an odour of burnt sugar, which became stronger with increase in temperature, but at no time disagreeable. On the addition of hydrochloric acid to the residue there was a brisk effervescence. The acid filtrate showed a slight trace of calcium.

A portion of the liquid extract was rendered alkaline with caustic potash solution, lime-water was added, and a precipitate formed on boiling. This was filtered off, redissolved, and re-precipitated with caustic potash and lime-water, confirming the test for citric acid.

The reaction for potassium was easily shown by wrapping a piece of platinum wire around a berry and holding it in a Bunsen flame.

The Tests for Atropine.—A small portion of the liquid extract was taken, and a solution of tannic acid added. The large brownish precipitate showed the presence of atropine. The precipitate was dissolved in hydrochloric acid and tannic acid was again added, when the brown precipitate again appeared. To another small portion of the liquid extract a solution of iodine in potassium iodide gave a precipitate of atropine. A solution of ammonium metavanadate in sulphuric acid gave a red precipitate, also a test for atropine. The fruit has long been noted for its large atropine content.

The sugar was examined by the time required for osazone formation with phenylhydrazine hydrochloride in the presence of sodium acetate. Two-tenths of a grm. of the dried sugar, three-tenths grm. sodium acetate, and 2 cc. of water were placed in a test-tube, which was immersed in a hot-water bath. The time of the osazone formation was noted. About fifty tests were made, and the time was between one and two minutes, indicating fructose. The osazone was purified by repeated crystallisation, and under the microscope showed the needle-like crystals which melted at 170°.

The Oils.—The nutlets contained in the 100 grms. of fruit were ground to a fine powder, placed in a Soxhlet apparatus, and treated with hot ether for seventy-two hours. About 10 cc. of oil was extracted. This was placed in a small open flask, and a portion seemed to evaporate after standing a few hours; that which remained possessed an odour resembling nut oil. About 400 grms. of the nutlets were next taken and extracted with ether as before; this gave sufficient oil for the tests. It was saponified with a solution of caustic potash. One portion of the oil remained liquid, while a second portion (after purification) became a solid. The melting-point of this indicated a mixture of palmitin and olein.

We desire to express our thanks to Professor N. Knight for suggestions and help in this work.

Chemical Laboratory, Cornell College,
October 2, 1907.

THE CATHODIC PRECIPITATION OF CARBON.

By WILLIAM BLUM and EDGAR F. SMITH.

SOME years ago one of us called attention to the electrolytic precipitation of iron, by the current, from citrate and tartrate solutions (Smith, *Am. Chem. Journ.*, x., 330; and *Journ. Analytical and Applied Chemistry*, v., 488). In doing so, mention was made that on dissolving the deposited metal "in dilute cold sulphuric acid a strong odour of hydrocarbons was perceptible." Later, reference was again made to this fact and conditions given, observing which, the contamination of the metal by carbon might be avoided (Smith's "Electro-chemical Analysis," 3rd Ed., p. 100). In electro analysis, the question of the contamination of metals by carbon, if the metals have been precipitated from organic electrolytes, has been quite freely discussed. However, the contamination in nearly all instances has been regarded as a result of carelessness in manipulation, and may be avoided.

During the past summer we made observations, on the conduct of certain organic acids under the influence of the current, which seem of value; hence a brief account of them is submitted in this communication.

To begin, it was tried to ascertain the degree of reduction of oxalic acid at the cathode. The gasometric method was called into use, *e.g.*, a comparison of the volume of hydrogen evolved in the cell with that liberated in a voltameter in the same period. It soon became evident that this procedure would not be delicate enough to detect any such reduction. However, while occupied in this way with an ammoniacal tartrate solution, a black deposit made its appearance on the cathode. When held in the flame it burned off completely from the platinum plate. The latter had an area of 100 sq. cm. Several actual trials may be here introduced. Thirty-seven and one-half grms. of tartaric acid were dissolved in water, neutralised one-half with ammonia, then diluted to a litre. Portions of this solution were electrolysed at a temperature of 60° C. The anode was a platinum spiral suspended in a porous cup. The cathode was the foil to which reference has been made. A current of 1 ampère and 12¼ volts acted for a period of two hours. A black deposit showed itself on the cathode. It burned off in the flame. In another experiment, with conditions like those just mentioned, discarding, however, the cup, there was no deposit on the cathode, but the solution was deep yellow in colour. Again, in electrolysing a portion of the ammonium tartrate without the porous cup, but surrounding the anode with a muslin bag, at the ordinary temperature, with a current of 4 ampères and 6 volts, there was a very considerable deposit, black in colour, on the cathode. It burned away, with the exception of a mere iridescence, when held in a flame. In another experiment, 15 grms. of tartaric acid were neutralised with ammonia, diluted to 150 cc., and electrolysed at 60° C., for four hours, with a current of 4 ampères and 6 volts. The anode and cathode had both been weighed. The cathode became coated with a greyish black deposit. The anode sustained a loss in weight, and only one-third of the cathodic deposit was carbon, the remainder being platinum, which had come from the anode.

Upon substituting a solution of citric acid (70 grms. to the litre) and electrolysing at 70° C., for three hours, with a current of 1 ampère and 16 volts, a heavy black deposit separated on the cathode. It was not affected by hydrochloric acid. It burned away completely in a Bunsen flame. The electrodes were separated by a porous cup. In other experiments a muslin bag surrounded the anode. This bag had previously been well soaked in caustic soda. The usual black cathodic deposit was obtained. It burned away completely on heating. On digesting this deposit with chromic acid, carbon dioxide was obtained and recognised by its reaction with lime water.

Another trial is worthy of notice. In it a half normal solution of ammonium citrate, made alkaline with ammonia,

was electrolysed for a period of five hours with a current of 4 ampères and 6 volts. The anode was protected by a muslin bag. The solution rapidly took on a yellow colour, a distinct odour of acetamide was evolved, and a black deposit appeared upon the cathode. It both burned on heating and generated carbon dioxide with a chromic acid mixture. It may be added that the solution was not heated from without as it developed a great deal of heat during the passage of the current.

Similar results were obtained on electrolysing a like solution without a diaphragm.

Other experiments were as follows:—

1. Five grms. of sodium citrate and 1 grm. of citric acid were dissolved in 150 cc. of water and electrolysed at 60° C., for five hours, with a current of 4 ampères and 11 volts. There was a brass-like deposit on the cathode. It weighed 0·0018 grm., while the anode had lost 0·0014 grm.

2. Fifteen grms. of citric acid, neutralised with ammonia and diluted to 150 cc., were electrolysed at 60° C., for four hours, with a current of 4 ampères and 6 volts. A greyish black deposit separated on the cathode. It equalled 0·0014 grm., which represents carbon. The anode lost in all 0·0103 grm. in weight.

In the many trials made, the solutions gradually acquired first a pale yellow colour, which in turn passed to brown and at times almost black without becoming turbid. However, it must be said that solutions of ammonium oxalate, ammonium formate, ammonium acetate, and ammonium succinate did not yield black deposits to the cathode. In solutions of ammonium lactate and benzoate they appeared as readily as in tartrate and citrate solutions.

This deposition of carbon upon the cathode is extremely interesting. In 1896, Coehn (*Zeit. Elektrochemie*, 1896, p. 541) called attention to the fact that when carbon was made an anode in the electrolysis of sulphuric acid, the latter became at first yellow, and by prolonging the experiment, dark red and reddish brown in colour. If this meant a solution of carbon the latter must presumably be in the form of ions, *e.g.*, in a form directable by the current. It must be in a form which, as it does not decompose water, would appear at the anode. With these thoughts before him, Coehn electrolysed sulphuric acid of varying concentration with an anode of carbon and a cathode of platinum. The result was a splendid deposition of carbon on the cathode. It burned away completely on heating, and gave carbon dioxide when acted upon with a chromic acid mixture. In later experiments, Coehn was able to determine in the electrolytic way the equivalent of carbon, and found it to be 3.

Turning to our observations with tartaric and citric acid, it must be that these are broken down at the anode during electrolysis; that the carbon thus liberated from combination in these acids enters aqueous solution as a hydrate of which the carbon is cation, and this, under influence of the current, passes in its ionic form to the cathode just as a metal in some salt does under similar influence. When, therefore, iron is deposited from a citrate or tartrate electrolyte, the carbon ions wander with the iron ions to the cathode, and there an alloy of iron and carbon appears. This alloy, on treatment with dilute sulphuric acid, generates hydrocarbons. Very little, if any, of the carbon deposited with iron is graphitic. It is chemically combined. Just as zinc and copper from certain electrolytes separate as brass, so do the carbon and iron separate as an alloy from the electrolytes which have been under discussion.

The conclusions warranted from the experiments here noticed, and many others like them, are:—

1. Carbon is deposited on the cathode from solutions containing tartaric, citric, lactic, and benzoic acids. This is particularly the case if a stationary anode be used along with high current density.

2. From solutions like those in 1, where high current density is employed, platinum will dissolve from the anode and be precipitated in part upon the cathode.—*Proceedings of the American Philosophical Society*, xlvi., p. 59.

THE MOLECULAR WEIGHT OF ARGENTIC SULPHATE, AND THE ATOMIC WEIGHT OF SULPHUR.*

By THEODORE WM. RICHARDS and GRINNELL JONES.

Introduction

THE atomic weight of sulphur has been investigated by many experimenters, but, as will be seen, the results are far from concordant. A brief review of these investigations forms the most appropriate introduction to the present one. The values in the following list have been re-calculated with modern figures for the other atomic weights involved (Ag = 107·93, Cl = 35·473, Pb = 206·9, Hg = 200·0, Na = 23·008, C = 12·002):—

1814	Berzelius (*Phil. Trans.*, civ., 20)	32·0
1826	Berzelius (*Pogg. Ann.*, viii., 15)	32·08
1833	Turner (*Phil. Trans.*, cxxiii., 539)	32·00
	Ditto	32·06
1836	Thomson (*Journ. Prakt. Chem.*, viii., 370)	32·
1844	Erdmann and Marchand (*Journ. Prakt. Chem.*, xxxi., 396)	31·99
1845	Berzelius ("Lehrbuch," 5th Ed., iii., 1187)	32·04
	Ditto	32·16
1848	Svanberg and Struve (*Journ. Prakt. Chem.*, xliv., 320	32·15
1851	Struve (*Liebig's Ann.*, lxxx., 203	31·94
1859	Dumas (*Ann. Chim. Phys.*, [3], lv., 148)	32·00
1860	Stas (*Bull. Acad. Belg.*, [2], x., 153, 322)	32·06 (*a*)
1878	Cooke (*Proc. Amer. Acad.*, xiii., 50)	32·137
	Ditto	31·980
1891	Richards (*Proc. Amer. Acad.*, xxvi., 268)	32·043
1898	Leduc (*Ann. Chim. Phys.*, [7], xv., 94)	32·056
1899	D. Berthelot (*Journ. de Phys.*, [3], viii., 271)	32·050
1904	Jaquerod and Pintza (*Comptes Rendus*, cxxxix., 129)	32·01
1905	Guye (*Comptes Rendus*, cxl., 1242)	32·065
1905	Jaquerod and Scheuer (*Comptes Rendus*, cxl., 1384)	32·036

(*a*) Van der Plaats (*Ann. Chim. Phys.*, 1886, [6], vii., 504 and 526) pointed out that Stas made an error in calculating his own data. Stas obtained 32·074, but 32·06 is correct.

The work of the predecessors of Stas is now of historical interest only, and does not merit detailed criticism; in recent times the atomic weight of sulphur has rested chiefly upon the experiments of the famous Belgian.

Stas converted silver into its sulphide by heating it in a current of sulphur vapour or hydric sulphide, but because he did not know the precautions necessary for preparing perfectly pure silver (Dumas, *Ann. Chim. Phys.*, 1878, [5], xiv., 289; Richards and Wells, *Publication* No. 28, 1905, p. 66), it is evident that all of his work in which silver was weighed needs revision. Stas also reduced argentic sulphate to silver in a current of hydrogen, but in this case he did not take the very important precaution of fusing the sulphate before weighing (Richards, *Proc. Amer. Phil. Soc.*, 1903, xlii., 28), and, moreover, the possibility that the reduced silver might contain argentic sulphide or sulphate was by no means excluded.

A brief review of subsequent work may not be out of place, although it is of a different order of precision. Cooke reduced argentic sulphide in a current of hydrogen, and concluded that the atomic weight of sulphur must lie between the limits 32·14 and 31·98. In summing up his results he stated that "this is equivalent to confirming the accepted value of this constant, so far as any experiments on a scale less extensive than those of Stas can be of value to this end" (Cooke, *Proc. Amer. Acad.*, 1878, xiii., 52).

The determination of the atomic weight of sulphur by Richards was made incidentally in his work on the atomic

* *Publication* No. 69, Carnegie Institution of Washington.

weight of copper. The ratio $Na_2CO_3 : Na_2SO_4$ gave as a result S = 32·075. If sodium is taken as 23·008 instead of 23·053, the result becomes S = 32·043. No very great confidence was placed in these results at the time, as is shown by the following sentence :—"The results are hardly capable of deciding the present uncertainty in the atomic weight of sulphur" (Richards, *Proc. Amer. Acad.*, 1891, xxvi., 269). It is probable that the result is too low, as no proof could be obtained of the thorough desiccation of the sodic carbonate.

Very recently numerous atomic weight determinations have appeared, depending on a purely physical method, based on the assumption that Avogadro's hypothesis and the simple gas law PV = RT is strictly true for gases when infinitely expanded. Since it is impossible to determine the ratios of the densities of gases with sufficient accuracy at very low pressures, it is necessary to determine this ratio under normal conditions, and apply a different correction in each case, depending on the deviation of the gas from the simple gas law. It is probable that the ratio of the densities can be, and in most cases has been, determined with sufficient percentage accuracy. On the other hand, the correction is hypothetical and much less certain, and, accordingly, the method has but little value when the correction is large.

According to Leduc the ratio between the densities of sulphur dioxide and oxygen is 2·04835 (*Comptes Rendus*, 1894, cxvii., 219). If no correction is applied for the imperfection of the gases, this value leads to 33·55 for the atomic weight of sulphur. The correction in this case is unusually large, and therefore must be known with a high percentage accuracy if the result is to have any value as a determination of atomic weights. The following are the general methods of calculating the correction, but none seems to be of sufficient value for the present case.

The first, called the "method of corresponding states," was developed for this purpose by Leduc (*Ann. de Chim. Phys.*, 1898, [7], xv., 5). It depends on the assumption of Van der Waals that two gases are in corresponding states, and deviate equally from the hypothetical perfect gas if their temperatures and pressures are equal multiples or sub-multiples of their critical temperatures and pressures respectively. In calculating the correcting factor, the compressibility and critical constants are used. Leduc (*Ann. Chim. Phys.*, 1898, [7], xv., 94) by this method obtained 64·056 as the molecular weight of sulphur dioxide, and 34·071 as the molecular weight of hydrogen sulphide, and hence from both S = 32·056.

The second method is the "method of critical constants" as developed by Guye (*Comptes Rendus*, 1904, cxxxviii., 1215; *Bull. Soc. Chim.*, 1905, [3], 5 Août; *Journ. Chim. Phys.*, 1905, iii., 321). The correction is calculated by the use of Van der Waals's equation, the quantities *a* and *b* being calculated from the critical constants of the gases under consideration. In a complicated manner Guye applied a correction to the quantities *a* and *b* of Van der Waals's equation, because they appeared to vary slightly with the temperature and the pressure (Guye, *Bull. Soc. Chim.*, 1905, [3], 5 Août, p. 12), and in this way was obtained the value 64·065 as the molecular weight of sulphur dioxide; hence, S = 32·065.

The third method is called the "method of limiting density." It was originated by Daniel Berthelot in 1898 (*Comptes Rendus*, 1898, cxxvi., 954, 1030, 1415, 1501; *Journ. de Phys.*, 1899, [3], viii., 263), and has been used by Rayleigh (*Phil. Trans.*, A, 1901, cxcvi., 205; 1902, cxcviii., 417; 1905, cciv., 352) and Jaquerod (Jaquerod and Pintza, *Comptes Rendus*, 1904, cxxxix., 129; Jaquerod and Scheuer, *Comptes Rendus*, 1905, cxl., 1384). It depends on the experimental determination of the compressibilities of gases at pressures in the neighbourhood of one atmosphere. By an extrapolation the "limiting ratio" of the densities at very low pressures can be calculated. This method has reached its greatest perfection in the hands of Lord Rayleigh, who has shown that for the permanent gases the deviation from Boyle's law only varies slightly with the pressure, and therefore the extrapolation is fairly safe. This physical method has been applied with the greatest success to the cases of hydrogen, carbon, and especially nitrogen, because in these cases the correction is comparatively small. Here, also, however, the application to sulphur is far less satisfactory. It is to be regretted that Lord Rayleigh's work did not include compounds of this element.

Jaquerod and Pintza determined the density of sulphur dioxide at 760 mm., 570 mm., and 380 mm. pressure, and from these results calculated the compressibility. The results were extrapolated to zero pressure on the assumption that the deviations from Boyle's law diminish as the pressure is lowered. They obtained 32·01 as the atomic weight of sulphur. Afterwards Jaquerod and Scheuer determined the compressibility of sulphur dioxide through the ranges 400 to 800 mm. and 200 to 400 mm. by a method similar to Lord Rayleigh's. They found, as was to be expected, that the deviation from Boyle's law was smaller at the lower pressure. Nevertheless, in calculating the molecular weight of sulphur dioxide, they assumed that the deviation from Boyle's law per centimetre of pressure between 0 and 760 mm. was the same as between 400 and 800 mm. They obtained 64·036 for sulphur dioxide, and hence S = 32·036. If their measurement of the compressibility through the range 200 to 400 mm. is used, the result becomes 32·052, and it seems probable that yet a higher value is the true outcome of their experiments. These different conclusions emphasise the uncertainty of the method.

Probably the adsorption of sulphurous oxide and hydric sulphide on the glass of the containing globes introduces an error in both the density and compressibility determinations, and hence in facts to which the assumption above mentioned are applied. This possibility of adsorption seems to have been not sufficiently heeded by any of the experimenters on sulphur compounds. It adds yet another uncertainty to the results.

The upshot of these considerations is the conclusion that none of the work heretofore done upon the atomic weight of sulphur decides its value. Hence further investigation is imperative. The problem, for complete solution, must be approached from many sides, and the work must involve many compounds of sulphur. The following contribution describes one section of a comprehensive programme by which it is hoped the question may be answered.

Preliminary Experiments.

The sulphate of silver was selected as the most suitable starting-point for the present investigation, because it seemed probable that this salt could be prepared in a pure condition and accurately analysed. A further reason for studying argentic sulphate lies in the possibility of later combining the results with some ratio involving the sulphide and thus furnishing evidence on the even more important question as to the atomic weight of silver. Balanced against the advantages is the disadvantage that only about 10 per cent of its weight is sulphur, causing the experimental errors to be greatly multiplied in the calculations, but the advantages more than outweigh the disadvantage.

A tentative preliminary plan of operations was to fuse argentic sulphate in a platinum crucible, dissolve it, precipitate as chloride, and collect and weigh the precipitate. This plan was thwarted by numerous obstacles. It was found that the sulphate decomposes slightly when fused, a difficulty which was later overcome. Again, the quantitative solution of the silver sulphate was a very tedious process. Eight grms. fused in a platinum crucible and placed in 1·5 litres of water required six weeks for its complete solution, even with frequent agitation. The action on the glass during this long time, the danger of the access of gaseous impurity, and the loss of valuable time all made this difficulty a serious one.

Argentic sulphate can be readily dissolved by placing twice its weight of concentrated sulphuric acid in the

crucible, and heating at about 300°; on cooling, the acid sulphate of silver crystallises out (Schultz, *Pogg. Ann.*, 1868, cxxxiii., 143). Upon adding water to this acid sulphate the normal sulphate is formed as a fine powder, which can readily be washed into the precipitating flask, and dissolved. The large excess of sulphuric acid thus introduced was far from desirable, however, for it tends to cause considerable occlusion of argentic sulphate in the precipitated chloride. In order to test this question, a solution, prepared as described above, and containing 7·4 grms. of argentic sulphate, was precipitated with hydrochloric acid. The precipitate was washed by decanting eleven times with very dilute hydrochloric acid, and then dissolved in ammonia and diluted. The argentic chloride was then re-precipitated with hydrochloric acid; the solution should contain all the sulphate previously occluded. After settling, this mixture was filtered, and the perfectly clear solution was evaporated in a platinum dish over an alcohol lamp until ammonic chloride crystallised out on cooling, the volume being then about 0·1 litre. To this were added about 10 grms. of baric chloride. An undoubted precipitate of baric sulphate was produced, which proved that there is considerable occlusion of sulphate by argentic chloride precipitated from solutions containing a large excess of sulphuric acid.

For the sake of comparison, approximately the same amount of argentic chloride prepared from nitrate was dissolved in ammonia, and 3·5 mgrms. of sulphate added. The solution was treated exactly like the preceding operations, and yielded about the same amount of precipitate. This experiment gives an approximate idea of the extent of the occlusion.

In searching for a means of wholly eliminating the sulphate it was found that a small proportion of argentic sulphate in argentic chloride could be completely converted into chloride by fusion in a current of hydrochloric acid gas. This observation led to the development of a new process in which the entire reaction was carried out in this manner, fused argentic sulphate being wholly converted into chloride without the need of dissolving in water. Thus the operation was greatly simplified, and the chances of error diminished.

The method of preparing the materials, the shape and nature of the apparatus, and many of the precautions and details of manipulation were adopted only after numerous preliminary experiments. A detailed account of this tentative work is, however, unnecessary, since the important results are implied in the description of the method which was finally adopted.

The Preparation of Pure Materials.

Sulphuric Acid.—The best commercial "chemically pure" acid was twice fractionally distilled, using a quartz condenser and a platinum dish as receiver. Only the middle fractions were used; 17 grms. left no visible or weighable residue on evaporation.

Argentic Sulphate.—Pure argentic chloride residues from previous atomic weight investigations in this laboratory were reduced with invert sugar and sodic hydrate. The reduced silver was thoroughly washed and dissolved in nitric acid, and the nitrate was diluted and filtered. It was evaporated on the steam-bath until saturated, and crystallised by adding an equal volume of concentrated nitric acid and cooling. The crystals were drained centrifugally as usual (Richards, *Journ. Am. Chem. Soc.*, 1905, xxvii., 104). The crystallisation from pure concentrated nitric acid and centrifugal draining was repeated five times, using Jena glass vessels. It was finally re-crystallised once more, using a platinum dish and re-distilled nitric acid. This silver nitrate was dissolved in a small amount of water in a platinum dish, and an excess of the purest sulphuric acid, diluted with an equal volume of pure water, was poured into it. The precipitated silver sulphate was drained in the centrifugal machine. It was then dissolved in hot concentrated sulphuric acid in a platinum dish, and the solution was boiled for several minutes to expel nitric acid. On cooling, the acid sulphate crystallised in large crystals. This acid sulphate was very thoroughly whirled, placed in a platinum dish, and treated with purest water. Heat was evolved, and the normal sulphate crystallised out as a fine powder. This powder was washed by decantation with the purest water until the wash-waters were no longer acid. (Unless this precaution is taken the silver sulphate cannot be dried thoroughly in the air-bath; in which case it would be impossible to clean properly the receiving end of the tube into which it was afterwards introduced; see below). All the water used in this work was purified in the manner described in previous communications. During this washing the action of light on the wet silver sulphate produces a slight violet colour. This, however, does no harm, as any slight decomposition is remedied during the subsequent fusion. It was then dried as much as possible in the centrifugal machine, and the drying was completed in an air-bath at 110°. These operations were carried out as much as possible under the protection of a very large inverted funnel, and the dish was kept covered with a large watch-glass, to avoid the introduction of dust. This sample was called A, and was used in the preliminary series, and in Experiments 4 and 5 of the final series of quantitative experiments.

Sample A was dissolved in concentrated sulphuric acid, boiled, crystallised as acid sulphate by cooling, centrifugally drained, converted into the normal sulphate by adding water, washed, and dried as before. This sample was called Sample B. Since the mean of the results with this sample is the same as the mean of Experiments 4 and 5, in which Sample A was used, it is evident that the boiling of the sulphuric acid solution followed by a crystallisation in two different crystalline forms did not affect the result; therefore further purification seemed unnecessary.

Hydrochloric Acid.—Hydrochloric acid, which was only used as a gas, was made from two sources. In Experiments 5 and 6 the hydrochloric acid was made by dropping pure sulphuric acid on pure ammonium chloride. In the other experiments the best commercial concentrated hydrochloric acid was used. Richards and Wells (*loc. cit*) have shown that this acid contained no other halogen or arsenic; it was therefore suitable for our purpose.

The Fusion of Argentic Sulphate.

Much thought was expended on the devising of a piece of apparatus which should be suitable not only for the fusion of argentic sulphate, but also for the quantitative conversion of the sulphate into the chloride. Finally, the simple symmetrical tube shown in Fig. 1 was found to be

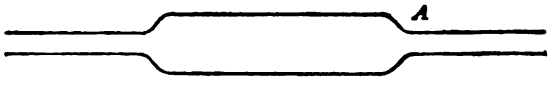

Fig. 1.—Quartz Tube used to contain the Argentic Salts. (One-half actual size).

best. It was the outcome of several trials and suggestions, and consisted of a thin cylindrical tube of fused quartz with smaller quartz tubes fused upon the ends. (We are greatly indebted to Prof. Baxter for his kindness in making this apparatus from a fine quartz tube and a quartz test-tube. To Mr. F. B. Coffin also we are indebted for a suggestion which led to a modification of the original shape of the tube). The tube was very light, weighing less than 6 grms. A very fine platinum-wire was wrapped many times around the constricted portion of the tube (A); by pulling this the tube could be readily rotated. It was hung on the balance in a horizontal position by means of a platinum-wire. The same tube was used throughout the research, the cylindrical shape giving it sufficient strength to withstand all the strains to which it was subjected.

The tube remained remarkably constant in weight in spite of the very vigorous treatment it received. During the entire fifteen experiments the loss in weight was only 0·41 mgrm., and during the twelve experiments of the final

series the loss was only 0·16 mgrm. This slight loss is probably accounted for by a slight solubility of the quartz in the concentrated ammonia or potassic cyanide solution used to remove the argentic chloride after each determination.

The sulphate of silver prepared as described above must have contained a little included water and excess of sulphuric acid, since it had been crystallised from an acid solution (Richards *Proc. Amer. Phil. Soc.*, 1903, xlii., 28). The only certain method of removing mother-liquor included within crystals is to fuse the salt. This part of the problem caused considerable difficulty; for it was found that argentic sulphate decomposes slightly when fused in air, becoming yellowish brown in colour. In order to decrease this thermal dissociation, the experiment was made of fusing the salt in a current of dilute sulphuric oxide, with complete success. The salt is then pure white in colour.

The small crystals of argentic sulphate were pushed into the tube with a platinum rod, and the narrow ends were freed from loosely adhering argentic sulphate by means of a clean feather tip, which had been previously washed with alcohol and ether to free it from grease. The tube was supported, on hooks of hard glass, in front of the apparatus for delivering sulphur trioxide. The very fine platinum-wire needed for rotating it had been wound around the tube in the first place.

The apparatus for delivering a current of pure dry air or sulphur trioxide or hydric chloride is shown diagrammatically in Fig. 2. A current of air was first driven over red-hot copper oxide (A) to remove organic matter, and subsequently through an Emmerling tower (B) containing beads moistened with a strong caustic potash solution. This tower was closed by a rubber stopper at the top, which introduced no impurity, since nothing but pure air passed over it. From this point, however, the apparatus contained no rubber connections or stoppers. All stopcocks were lubricated with phosphoric or sulphuric acid.

The air was dried by passing through two Emmerling towers (C and D) containing beads moistened with concentrated sulphuric acid. The current of air could then be either used in a pure dry state by passing through L or F, or else charged with sulphur trioxide by bubbling twice through fuming sulphuric acid in the bottle E. This acid was kept saturated by an excess of solid sulphur trioxide. A current of air mixed with any desired proportion of sulphur trioxide was thus delivered through G into the quartz tube H. The delivery tube, G, and the quartz tube, H, touched each other, but no attempt was made to secure a tight joint.

The argentic sulphate contained in the quartz tube was then fused with a fish-tail Bunsen burner held in the hand. A red heat is required. When all of the sulphate was fused, the stopcock, P, delivering sulphur trioxide was closed, and a rapid current of air was admitted through F. As soon as the fumes of sulphuric acid could no longer be seen escaping from the end of the quartz tube, the flame was removed, and the tube was slowly rotated by drawing out the platinum-wire wrapped around one end. This causes the argentic sulphate to solidify in a thin sheet around the tube. Unless care is taken to keep the salt at least 1 cm. distant from either of the end tubes, difficulty is experienced during the conversion into chloride.

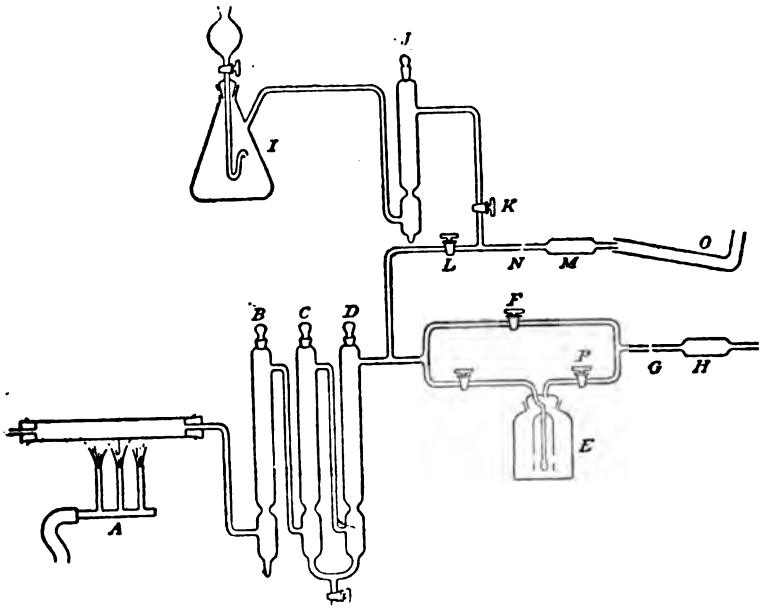

Fig 2.—Apparatus for Delivering appropriate Gases into the Quartz Tubes.

The final solidification in the current of pure dry air was carried out very rapidly, in order to avoid decomposition and obtain a perfectly white sample. If the argentic sulphate was kept fused ten or fifteen seconds too long after the sulphur trioxide current was stopped, a yellowish brown product was obtained. This indicates that the salt contained either metallic silver or argentic sulphide. Richards, Wells, and Forbes have shown that a slight discolouration of a fused silver salt is a very delicate test for impurity (Richards and Wells, *Carnegie Inst. Pub.* 28, 1905, xxviii., 31; Richards and Forbes, *Carnegie Inst. Pub.* 69, 1907, p. 55). The loss of weight due to this discolouration was very slight, as will be shown below.

The entire tube was later heated in a current of pure air at a temperature above the boiling-point of sulphuric acid for about five minutes, in order to drive out any possible accidental trace of acid in the tube. While still warm it was placed in a desiccator, and later weighed. The tube was kept horizontal until the end of the experiment, to avoid any chance of mechanical loss.

The device of spreading the salt in a thin layer around the tube by rotating the tube during the cooling had four very important advantages:—First, the chance of breaking the very fragile quartz tube during the solidification and cooling was greatly reduced by the more even distribution

of the strain; secondly, the salt was agitated and spread out in a thin layer while still fused in a current of pure air, thus facilitating the escape of any possible trace of dissolved sulphur trioxide; thirdly, the cooling was made more uniform and rapid, so that the argentic sulphate had no time to decompose before it had solidified; and fourthly, a much larger surface was exposed to the later action of the hydrochloric acid.

The possibility just mentioned that the colourless argentic sulphate might contain an excess of sulphur trioxide needed careful consideration. Unfortunately, a direct test for acid seemed to be impracticable, owing to the slight solubility of silver sulphate; hence light upon the question was sought in several distinct ways.

Weber (*Ber.*, 1884, xvii., 2503) has found that in order to prepare a compound $Ag_2S_2O_7$ argentic sulphate must be heated with sulphur trioxide under pressure in a sealed tube. This, together with the fact that argentic sulphate decomposes so easily when fused, indicates that it does not have a great tendency to retain sulphuric oxide, and that the vapour tension of the trioxide in the disulphate is far above that maintained in the present experiments. In order to obtain quantitative evidence, the pure white sulphate in six of the final experiments, after being weighed, was fused again for about ten to fifteen seconds in order to decompose it slightly. This gave a slight but unmistakable dark colour to the salt. The resulting losses of weight are here tabulated:—

The Loss of Weight caused by slight Decomposition.

Experiment No.	White Ag_2SO_4.	Darkened Ag_2SO_4.	Difference.
9.	5·27714	5·27709	0·00005
10.	5·16313	5·16302	0·00011
11.	5·08383	5·08377	0·00006
12.	5·13372	5·13367	0·00005
13.	5·16148	5·16138	0·00010
15.	5·37436	5·37425	0·00011
		Average	0·00008

The loss in weight was thus on the average only 0·08 mgrm. or 0·0015 per cent. It seems certain that at least part of this loss in weight was due to a deficiency of either oxygen or sulphur trioxide in the darkened sulphate, and not to the loss of an illegitimate excess of the latter substance. Therefore, although it may be a debatable question as to whether it is safer to take the weight of the white or darkened samples as the true weight, it seems probable that the weight of the white sample was more trustworthy. Even at the worst the uncertainty cannot have been greater than 0·001 per cent. This result agrees with the earlier conclusions already cited concerning the obvious effect of very slight decomposition on the colour of silver salts. It appears that in the present case, as in the others, the slight stability of these compounds is a real assistance in the production of a typical compound, instead of a hindrance to precise quantitative work.

For weighing the argentic sulphate, and of course the chloride also, the Troemner balance which had served in many similar researches was used (Richards, *Proc. Amer. Acad.*, 1891, xxvi., 242). The Sartorius platinised brass weights were standardised by the usual Harvard method (Richards, *Journ. Am. Chem. Soc.*, 1900, xxii., 144).

As usual, all weighings were made by substitution, a make-weight being placed on the right-hand balance pan. In order to avoid as far as possible any error due to changing meteorological conditions, a substituting counterpoise of the same material and approximately the same surface and weight was used. Every weighing was repeated, and the successive values seldom differed more than 0·03 mgrm. No difficulty was experienced from hygroscopic adsorption of water by either argentic sulphate or argentic chloride, except on a few days when the air was unusually humid. In these cases the tube was heated to about 330°, and allowed to remain in a desiccator until the conditions were more favourable. The tube was always allowed to remain at least three hours in a desiccator near the balance before making a weighing, and during this time was covered by a black cloth to protect the sensitive salts from the light.

In order to correct the weights to the vacuum standard, the specific gravity of argentic sulphate is needed. Following are the published results concerning this datum:—

Density of Argentic Sulphate.

Karsten (*Schweigger's Journ.*, 1832, lxv., 419) ..	5·341
Playfair and Joule (*Mem. Chem. Soc.*, 1845, ii., 430)	5·322
Filhol (*Ann. Chim. Phys.*, 1847, [3], xxi., 417) ..	5·410
Schröder (*Pogg. Ann.*, 1859, cvi., 245)	5·425
Petterson (*Upsala Nova Acta*, 1874, [3], ix., 35)..	5·49 5·54

After a study of the original papers, the value 5·45 was provisionally adopted as the most probable value, but, as there was some doubt about its accuracy, this was verified by experiment.

The density of the toluol to be displaced by the salt was determined by means of an Ostwald pycnometer at 29·2° to be 0·8566 (the mean of three concordant determinations); 6·067 grms. of previously fused silver sulphate were found to displace 0·9532 grm. of this toluol, and therefore occupied 1·113 millilitres (the mean of two determinations). Hence the density of argentic sulphate is 5·45, as supposed. This involves an additive correction of 0·0000775 grm. to each apparent grm. of the salt, a value which is decreased 0·0000011 by an increase of a centimetre of atmospheric pressure, or decreased 0·00000026 by an increase of a degree of temperature. The correction to the weight was applied accordingly.

(To be continued).

THE

USE OF FELSPATHIC ROCKS AS FERTILISERS.*

By ALLERTON S. CUSHMAN,
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Introduction.

IN view of the great demands that are being made upon the agricultural resources of the country, it is a matter of vital importance that consideration be given to the available supplies of elements which are necessary to sustain and maintain the quality and quantity of the crops. It is well known that there are three principal fertilising materials—nitrogen, phosphoric acid, and potash. The discovery of electro-chemical and bacteriological processes for fixing the nitrogen of the air, thereby changing it into a form in which it can be used as a plant food, seems to remove all doubt as to the abundance of the supply of this important element for all time to come. An enormous geographical area of this continent is underlain with practically inexhaustible supplies of phosphatic rock, which, with the phosphates obtainable in waste bone, slaughterhouse tankage, fish scrap, and the basic slags from the iron industry, insure a limitless supply of phosphoric acid.

With regard to potash alone there has been reason to feel anxiety. Up to the present time no deposit or source of this necessary element in any of the forms in which it has been heretofore considered available as a plant food has been discovered or developed in this country. The mines of Stassfurt, Germany, furnish almost the entire supply of potash for fertiliser in the United States, exclusive of that which is used over and over by the processes of natural and green manuring. The potash salts which up to this time have been exclusively used for fertilising consist of muriate, sulphate, nitrate, and carbonate, either in a crude or in a previously purified condition. Kainite

* From *Bulletin* No. 104, U.S. Department of Agriculture, Bureau of Plant Industry.

TABLE I.—*Imports of Potash Salts for Use as Fertilisers.*

(Compiled from data furnished by the Bureau of Statistics, U.S. Department of Agriculture).

Kind of fertiliser.	1903.		1904.		1905.	
	Weight (lbs.).	Value (dols.).	Weight (lbs.).	Value (dols.).	Weight (lbs.).	Value (dols.).
Crude carbonate ..	11,130,789	141,033	8,193,872	224,396	7,166,569	218,816
Crude muriate . ..	172,838,780	2,630,457	161,503,735	2,428,480	202,366,601	3,241,152
Crude nitrate	11,946,685	320,082	16,727,175	433,626	14,512,306	386,098
Crude sulphate . ..	45,156,964	782,082	47,592,131	833,954	54,577,670	958,305
Kainite	553,875,840	1,080,393	356,124,160	839,382	539,369,488	1,143,296
Total	794,949,058	4,954,047	590,141,073	4,759,838	817,992,634	5,947,667

is a trade name given to a crude product of the German mines which contains about 13 per cent of actual potash, largely in the forms of sulphate and chloride (muriate). The quantity and value of potash salt to be used as fertilisers imported in the fiscal years 1903, 1904, and 1905 are shown in Table I. The price of the potash unit has shown a tendency to increase each year.

All of the above salts of potash are readily soluble in water, and therefore become quickly available as plant food when applied as fertilisers. On the other hand, the acids with which the potash is combined in these salts, especially in the cases of the sulphate and chloride, are absorbed only in extremely minute quantities by growing plants. The natural consequence of this is that, as the potash is taken away year after year, the acid elements collect, in some cases to the great detriment of the soil.

Potash in some form is absolutely necessary to the successful growth of all crops, and is found in varying degrees in the ashes of wood and of vegetable growths of all kinds. This is illustrated in Table II., in which analyses of ashes of a number of vegetables are given. It must be remembered, however, that the amounts of this element found in the ashes of plants vary greatly under different conditions, and that the sap of plants frequently absorbs much more of a given element than is actually necessary for its growth. The important point is that potash is an essential plant food of all crops, and particularly of those species which are starch builders.

TABLE II.—*Analyses of Vegetable Ash.*

Ash.	Phosphoric acid, P_2O_5.	Potash, K_2O.	Soda, Na_2O.
	Per cent.	Per cent.	Per cent.
Pea	36	40	1
Bean	30	44	1
Potato	19	59	2
Parsnip	18	36	5
Carrot	12	36	13
Cabbage	16	48	4
Turnip	13	39	5
Artichoke	16	65	2
Tobacco	15	49	11

We can trace the source of potash in all its forms and wherever found to the igneous rocks which constituted the original crust of the earth. From the averages obtained from the analyses of a large number of crystalline rocks of common occurrence found in this country, Clarke (*Bull.* 228, U.S. Geol. Survey, p. 20) has made the following calculations of the relative abundance of various rock-forming minerals :—

	Per cent.
Apatite (phosphate of lime)	0·6
Titanium minerals (oxides and silicates)	1·5
Quartz (silica)	12·5
Felspar (silicates of aluminium, potash, soda, and lime)	59·0
Biotite mica (silicates of aluminium, magnesium, potash, &c.)	3·8
Hornblende and pyroxene (complex silicates) ..	16·8
Miscellaneous	5·8
Total	100·0

It is seen from this that probably the majority of all the original rocks contain more than 50 per cent of felspar. There are, however, a great many different varieties of felspar. The felspars belong to a type of minerals known as silicates, in which aluminium and other elements, such as potash, soda, and lime, are combined with silica. Pure orthoclase felspar is a silicate of aluminium and potash, which theoretically should contain 16·8 per cent of potash(K_2O). As a matter of fact, it is extremely difficult to find an example of pure orthoclase, and in most of the felspars, which occur in large deposits, the potash is to a greater or less extent replaced by soda or lime, or both. For this reason it is impossible to tell without a chemical analysis how much potash any given felspar will contain. The granite rocks consist of felspar, quartz, and a little mica in varying proportions; many of the other well-known rocks, such as the slates, sandstones, gneisses, and traps, also frequently contain more or less felspar. Some of these rocks carry little or no potash, although many of them will run as high as 5 per cent; very few of them run higher than this.

A cubic foot of granite weighs about 170 pounds; on a 5 per cent basis, 8·5 pounds of this is potash. A quarry 100 feet square and 100 feet in depth of such rock would therefore contain 8,500,000 pounds of potash (K_2O). It is at once apparent that nature offers a limitless supply of raw material which only awaits an economical process to make the potash available.

In many localities there occur large dikes or deposits of more or less pure felspars, which usually run higher in potash than the true granite rocks. These large deposits, which occur in a great many of the States, have been developed in Maine, Connecticut, Pennsylvania, New York, and Maryland, where they have been mined extensively and the felspar ground to fine powder, principally for use in potteries. As has been said, pure orthoclase felspar should contain 16·8 per cent of potash (K_2O), but none of these deposits will run on the average much more than 8 to 10 per cent. For pottery use it is essential that the spar should melt in a kiln fire to a clear white glass, and it must therefore be almost entirely free from mica or iron-bearing minerals. For this reason there are large quantities of materials at every felspar quarry which, though unfit for pottery use, would be valuable if any method were known of making potash available.

The question whether fine-ground felspar can be used as a potash fertiliser has been a matter of controversy for many years. There is a large and widely scattered literature on the subject, an examination of which shows that the matter has been debated with much vigour, and sometimes with prejudice and intolerance on both sides. It is easy to find the published records of a number of experiments, made by trained and thoroughly competent agriculturalists, which tend to show that ground felspar is an efficient potash fertiliser. On the other hand, a number of experiments seem to indicate that the potash is only slightly available, while others would appear to show that the ground rock is entirely useless. On account of the large interests involved in the settlement of this question it is not difficult to see why vigorous differences of opinion, and even unjust prejudice, should have arisen. When, however, trained investigators reach opposite conclusions,

based upon experimental evidence, we are forced to the opinion that while ground felspar may be a useful fertiliser under certain conditions it is not so under others.

It is the object of this *Bulletin* to present and discuss as fully as possible all the evidence that can be obtained on both sides of this important question. The great demand for information on the subject which has arisen and the numerous misstatements that have been printed make it desirable to present the evidence obtained up to date, even though many more years will be necessary for the conclusion of careful systematic investigation under crop and field conditions.

The availability of potash contained in felspathic rock must depend upon several important considerations, which can best be expressed by a discussion of the following questions:—

1. Is the potash locked up in felspar and the felspathic rocks, such as granite, gneiss, rhyolite, syenite, &c., to any extent available as a fertiliser when these rocks are crushed or ground to fine powder?

2. If the first question can be answered in the affirmative, what influence does fineness of grinding have on the question, and to what degree of fineness is it necessary to grind in order to make a sufficient amount of potash available in the first season after application?

3. What would be the cost of using ground rock in place of the soluble compounds which up to the present time have been exclusively used, and would there be economy in so doing?

4. Could any subsequent damage result from the use of ground rock; and if so, how would such damage compare with that which follows the continued use of soluble compounds, such as chloride, sulphates, and carbonates?

5. If it should be determined that the potash in ground felspathic rock is only partially available as a fertiliser, is there any method or process by which the ground rock could be treated so as to increase this availability?

(To be continued).

SYNTHETICAL CHEMISTRY IN ITS RELATION TO BIOLOGY.*

By Prof. EMIL FISCHER, F.R.S.

Exactly forty years are elapsed since Faraday's death, and already, on eight occasions, discourses in honour of his memory have been delivered, at the instance of this Society, by distinguished representatives of the sciences which he did so much to forward. Most of them, mindful of Faraday's discoveries, have dealt with general problems connected with our fundamental conceptions of matter and its inherent forces, so that, when honoured with the invitation to deliver the ninth of these lectures, I could not but feel sensible of the difficulty of following the example of my predecessors, as the field in which I have sought to enlarge the boundaries of knowledge is one far removed from such considerations.

In Faraday's time, it is true, the labours of workers in the natural sciences were not specialised as they are now; his genius was such, however, that, although not trained in its service, he was able to enrich organic chemistry with observations of momentous consequence. I need but allude to his discovery of benzene: the practical importance of this substance and its dominant position in the host of carbon compounds with which we are now acquainted were generally recognised in the course of the celebration held in this room, only fifteen months ago, in honour of Sir William Perkin.

But in the course of his labours as an investigator Faraday never approached the attractive problems which organic chemistry affords on its biological side. I must therefore crave your indulgence in selecting this theme in particular as the subject of my address. Happily, I am sustained by the conviction that biology, on account of the breadth and importance of its aims, may claim to rank with the inorganic sciences, although perhaps it lacks their exactness of method; nowhere can it count on fuller recognition of its achievements and of the importance of its problems than among the countrymen of Charles Darwin.

It is easy to understand why in its early youth organic chemistry was so closely connected with biology; the materials which the chemist was called upon to investigate were mostly products of animal or vegetable origin. Indeed, carbohydrates, proteins, and vegetable acids served Lavoisier, Gay-Lussac, Berzelius, and Liebig as materials in elaborating the methods of elementary analysis.

The isolation of urea from animal urine by Rouelle, the recognition of uric acid, lactic acid, malic acid, and glycerin by Scheele, the isolation of asparagin by Vauquelin and Robiquet, of morphine by Serturnier, together with many other similar discoveries accomplished during the first ten years of the nineteenth century, are admirable examples of the manner in which the living world was drawn upon and made to yield up its treasure of chemical compounds. The many hundreds of natural organic compounds enumerated in the text-books of animal and vegetable chemistry are proof of the rich harvest since gathered in this field of investigation. But how small is their number when compared with the 130,000 carbon compounds which organic chemistry can boast of to-day. All these, it is known, are either products of the artificial transformation of organic matters occurring naturally or have been completely synthesised from their elements. The accumulation of this huge material, including the elaboration of the necessary methods, has been the main occupation of organic chemists during the past sixty years; and as their discoveries gave rise to much happy speculation, for the time being they took the lead in developing chemical theory.

It is not to be denied that, in the latter half of the last century, owing to the growth of the subject in importance, organic chemistry became separated from biology. It cannot be mere chance that the most famous of Liebig's pupils, A. W. Hofmann, A. Kekulé, and A. Wurtz, did not follow the example of their great teacher, whose chief triumphs were won by the use he made of chemical methods in solving biological problems. Perhaps they were restrained by the feeling that, mainly through his influence, physiological chemistry had been developed into a separate discipline, which should be cared for by men who could devote themselves entirely to its service. Such subdivision of labour undoubtedly has many advantages; the disadvantages would have outweighed these had it precluded interchange of experiences and friendly co-operation of workers in the two fields; the history of both sciences, however, affords ample proof that such has not been the case.

Physiologists have ever been ready to avail themselves of the latest developments of chemical analysis and synthesis, whilst organic chemists have not only been stimulated in many ways by biologists, but their studies have derived much practical aid from biological science. I may instance the modern development of the chemistry of fermentation, which began with the pioneer work of Pasteur and was greatly favoured by the introduction of Koch's refined bacteriological methods; also the flourishing industry to which the manufacture of medical remedies prepared by synthetic methods has given rise.

But organic chemistry will certainly never be content to act as the mere handmaid of biology. This is impossible, as the theoretical and technical problems which she is already called upon to consider are too numerous and they cannot fail to increase in number and importance in the future. But I do consider it not only possible but desirable, that the close connection of chemistry with biology which

* Faraday Lecture, delivered before the Chemical Society, October 18, 1907. From the *Transactions of the Chemical Society*, 1907, vol. xci.

prevailed in the days of Liebig and Dumas should be re-established, as the great chemical secrets of life are only to be unveiled by co-operative work. I will therefore attempt to indicate the part chemistry can play by references to cases of which I can claim to have personal experience.

We know that in nature the construction of organic matter begins in the leaves of plants with the conversion of carbon dioxide into sugar, from which many physiologists suppose the complex substances contained in the living cell are formed by further changes in which nitrogen, sulphur, and phosphorus take part.

These transformations are for the most part enveloped in mystery. We know nothing definitely even of the assimilation of carbon dioxide. Of the various hypotheses advanced to explain the change, that advocated by A. von Baeyer has gained most support, namely, the view that the initial product is formaldehyde, glucose being formed from this by a process of polymerisation. Actually both changes have been effected artificially. After it had been shown by Butleroff that on heating formaldehyde with lime water a sugar-like, syrupy product is formed, and O. Loew had improved the method of effecting the condensation, I was able to adduce proof that the complex mixture contains a small quantity of an α-acrose which can be transformed into glucose. As it was known that carbon dioxide could be converted into formaldehyde by more or less drastic means, the preparation of glucose from carbon dioxide thus became a possibility. Recently, Fenton has succeeded in carrying out the reduction of carbon dioxide to formaldehyde at a low temperature in aqueous solution, so that it is now possible to effect the complete synthesis of sugar at temperatures such as prevail in the living plant. But how thorough is the work of the plant in comparison with our laboratory practice; usually when such questions are discussed, the poor yields which our methods give rise to are forgotten!

I need only allude here to recent apparently successful attempts, on the one hand, to effect the reduction of carbonic acid to formaldehyde by means of light and, on the other, to detect formaldehyde in green leaves, as Professor Meldola dealt exhaustively and critically with these questions in his Presidential Address eighteen months ago. I may be allowed, however, to dwell somewhat on one peculiar feature of the natural change, namely, the asymmetric character of the synthesis; according to present experience, and especially the brilliant investigations of H. Brown and Morris, the optically active hexoses of the *d*-series, glucose and fructose, are alone formed.

But from the experience gained in effecting syntheses in the sugar group, as I showed some time ago, it is possible to give a fairly satisfactory explanation of this change. It is only necessary to assume that the condensation is preceded by the formation of an additive compound of formaldehyde with some optically active constituent of the chlorophyll granules. I shall give a more precise form to this hypothesis if I say that I consider it probable that the carbon dioxide itself enters into combination in this manner, as there is reason to suppose that the proteins offer sufficient opportunity for its fixation; according to Siegfried, even the simple amino-acids are capable of combining with carbon dioxide. I am inclined to think that this compound with carbon dioxide undergoes decomposition into oxygen and a reduction product, probably a derivative of formaldehyde; the condensation to sugar takes place either in the original asymmetric complex or in one produced from it by a secondary change involving the separation of the formaldehyde and its re-association in some other manner. It may be that the condensation takes place directly or that intermediate compounds, biose or glycerose, are formed. Thanks to the researches of Marckwald and especially those of Mackenzie, we are acquainted with a whole series of asymmetric syntheses; no one of these, however, is half so complete as that involved in the formation of sugar under natural conditions. Indeed, it is obvious that if the natural process is to be imitated *in vitro*, it will be necessary to alter the methods hitherto adopted in every single detail; difficult as this may appear, it is not altogether impossible.

But even if this be done successfully, the precise nature of the assimilation process will not be finally elucidated. It is to be expected that this will only be accomplished when biological research, aided by improved analytical methods, has succeeded in following the changes which take place in the actual chlorophyll granules.

The carbohydrates elaborated by the plant undergo combustion to carbon dioxide and water in the animal body. The change is easily effected by means of powerful oxidising agents at the ordinary temperature; the natural process, however, must be a very different one, as in the organism oxygen is conveyed to the carbohydrate by oxidising enzymes and doubtless many intermediate products are formed of which we know little at present.

It would be easy to multiply examples. But these two are sufficient to demonstrate the incompleteness of the explanation of biochemical processes deduced from the data of organic chemistry. The service rendered to biology by chemical analysis and synthesis which will be rendered by it in even greater measure in the future, is to be sought in other directions.

The ultimate aim of biochemistry is to gain complete insight into the unending series of changes which attend plant and animal metabolism. To accomplish a task of such magnitude, complete knowledge is required of each individual chemical substance occurring in the cycle of changes and of analytical methods which will permit of its recognition under conditions such as exist in the living organism. As a matter of course, it is the office of organic chemistry, especially of synthetic chemistry, to accumulate this absolutely essential material. The chemical constitution of hundreds of carbon compounds which occur naturally has already been determined and their more important properties have been established. But far more remains to be done. In proof of this, let me briefly direct your attention to the three great classes of substances which predominate in the living world: the fats, the carbohydrates, and the proteins.

It was established at least ninety years ago by Chevreul, in the course of his celebrated investigations into the process of soap-making, that the fats can be decomposed into the glycerin discovered by Scheele and into fatty acids; but the relationship of these latter to one another could not be understood until the conception of homologous series had been evolved in organic chemistry. The classical researches of Berthelot and the discovery of glycol by Wurtz were necessary preliminaries to the establishment of the constitution of glycerin; the final proof that the fats are neutral glyceric salts of the fatty acids was first provided by Berthelot's synthesis. Synthetic methods have made us acquainted with the mono- and di-glycerides and also with mixed triglycerides such as have frequently been met with of late in nature.

Nevertheless, the group in which the natural fats are ranged is one in which there are still many lacunæ and many mis-statements to be corrected. Fatty acids of high molecular weight, which for years were regarded as entities, such as margaric acid, are now acknowledged to be mixtures; others, like the cerotic acid of bees-wax, have received new formulæ; in fact, the higher acids and the oxy-acids all require to be studied afresh, and, whilst it is true that the general constitution of the fats is known with certainty and the quantitative composition of the most important natural mixtures is established with a fairly satisfactory degree of accuracy, yet there is much uncertainty on the physiological side; even such an apparently simple problem as that involved in the determination of the manner in which fats are absorbed in the animal intestine has not yet been definitely solved. Although enzymes capable of cleaving fats are known to be present in the secretions of the stomach and pancreas, opinions are still divided as to whether the fat is absorbed

in a state of fine emulsion or whether it first undergoes hydrolysis.

Still less is known of the manner in which fats undergo combustion to carbon dioxide and water in the animal body. Hitherto this change has been imitated artificially only at relatively high temperatures. It is obvious that it would be of far greater interest to discover oxidising agents which would produce the effect at low temperatures. No doubt many intermediate products would be met with and the study of these would afford valuable assistance to biologists in devising experiments with animals.

The formation of fats in plant and animal tissue is no less complicated a phenomenon. It is certain that carbohydrates are the chief source of supply. We know next to nothing, however, of the actual course of this remarkable synthesis; it is easy to imagine that glycerol may be formed by the hydrolysis of glucose and that three molecules of glucose may give rise to an acid containing eighteen carbon atoms. But the process involved in the conversion of sugar which is rich in oxygen into fatty acids containing little oxygen remains wrapped in mystery. I imagine that this change, like that which attends alcoholic fermentation, is effected by a rearrangement of oxygen atoms within the molecule and that it involves the elimination of carbon dioxide. To imitate such a process artificially, of course, is an attractive problem to be dealt with from the synthetic side; but it is doubtful if it can ever be solved by purely chemical methods. In all probability, the organism has at its disposal for the purpose a number of enzymes which effect the complete synthesis in a series of interactions following rapidly one upon another.

The problems offered by the fats are simple, however, in comparison with those connected with the carbohydrates. The original subdivision of the group into mono-, di-, tri, and poly-saccharides has been justified in practice. Up to the present time only the monosaccharides have been studied satisfactorily from the point of view of their spatial structure. The dogma which at one time prevailed that Nature produces only carbohydrates with six atoms of carbon was upset by Kiliani's discovery that arabinose contains but five atoms of carbon. Since then the group of the mono-saccharides has been so extended by synthetic means that sugars of all types, from glycollic aldehyde (biose) to the nonoses, are now known, the group including besides the seven compounds which occur naturally no less than forty-five synthesised products.

Our knowledge of this group is also fairly satisfactory from the stereochemical standpoint, as the greater number of the isomerides predicted by theory as well as the more important aldohexoses and aldopentoses have been prepared and their inter-relationship can be expressed by steric formulæ. Similar results have been arrived at in the case of the great class of glucosides, the synthesis of the most simple representative from glucose and methyl alcohol having led to the discovery of both the theoretically possible stereoisomerides.

The growth of our knowledge of the monosaccharides has proved in many ways to be of importance in connection with biological inquiry, especially in enabling us to penetrate the mystery of enzyme action somewhat further.

On contrasting the effects which emulsin and the enzymes in yeast produce on the various glucosides prepared by synthetic methods, I was led to conclude not only that there was a difference between the two series of optical antipodes similar to that discovered by Pasteur in the course of his studies of moulds, but that very slight changes in configuration were sufficient to inhibit the action of enzymes entirely. I was led by these observations to apply the simile of *lock* and *key* as an expression of the close inter-relationship in configuration which obtains between the enzyme and the substance which it attacks.

Similar results were obtained on investigating the behaviour of the stereoisomeric hexoses with yeast, the fermentative power of which we now attribute to an enzyme: E. Buchner's zymase.

The experience gained with the glucosides became of service in studying the polysaccharides; for example, maltose and milk-sugar were found to differ in their behaviour towards the enzymes of yeast and emulsin much as do α- and β-methylglucoside. Another outcome of the investigation has been the discovery of distinct enzymes capable of attacking di- and tri-saccharides. Thus lactase was found to be present in Kefir grains and milk-sugar yeasts and definite proof was given of the presence of a maltase in beer yeast. As the result of these inquiries, I was able to formulate a rule of general biological significance, namely, that the alcoholic fermentation of a polysaccharide is necessarily preceded by its hydrolysis by some particular enzyme. It was shown, especially in the case of the invertase of *Monilia Candida*, that it is not essential that the enzyme should even be soluble in water. I may mention here that E. Buchner has himself admitted that he was led by these observations on *Monilia* to make his experiments on the mechanical separation of zymase from the yeast cell.

Unfortunately but few successful syntheses of polysaccharides have been effected. Musculus obtained dextrin-like products from grape-sugar by treating it with mineral acids; and I have shown that a disaccharide, *iso*maltose, may be produced in this way. E. Frankland Armstrong and I have prepared a number of disaccharides by synthesis from the acetylchlorohydroses; one of these products, probably, is identical with mellibiose.

But methods such as I refer to are so difficult in their application that their use cannot well be extended to any large number of polysaccharides. It is most desirable therefore that better methods should be devised, as it is probable that the attack on the dextrins, gums, and similar undeciphered substances is most likely to be successful if made from the synthetic side. It is to be expected that biology would gain much by the discovery and utilisation of such materials; more, perhaps, than it has from the study of the mono-saccharides and of the glucosides prepared by artificial means.

The carbohydrate group is that in which use was first made of enzymes as synthetic agents. You are aware that Croft Hill succeeded in preparing complex carbohydrates by subjecting glucose to the action of the enzymes in beer yeast. His contention that the product is maltose has been controverted; it is more probable that the condensation which glucose undergoes under the influence of the enzyme resembles that effected by hydrogen chloride, that is to say, that the product is a mixture of *iso*maltose with non-fermentable dextrins. In any case, Croft Hill has the great merit of having been the first to demonstrate the reversibility of enzyme action, and since his experiments were made similar results have been obtained with other enzymes, lipase, for example.

An important extension of Croft Hill's discovery is afforded by E. F. Armstrong's observation that the action of emulsin is different from that of the enzymes of yeast, the condensation of glucose taking place in such a way that a disaccharide which appears to be maltose is formed together with other complex products. Such syntheses effected by the agency of enzymes fascinate the imagination, as they approximate closely to natural processes; but I may point out that they cannot take the place of purely chemical methods, as these latter are so much more under our control, and can be varied in so many ways that we are in the position to produce materials which it is quite impossible for the organised world to furnish. Laboratory synthetic methods will be indispensable for a long time to come, not only for preparative purposes but also as the means of elucidating the structure of complex substances of natural origin.

This contention is applicable to the proteins even more than it is to the carbohydrates; as they are among the most complex substances produced in the living world, and are concerned in all the vital activities of the cell, a complete comprehension of their nature must obviously precede

the full development of biological chemistry. I may therefore be allowed to give very briefly a rapid survey of the present position of the chemistry of the proteins. The investigation necessarily began with the isolation and classification of the natural materials, and these were subdivided according to purely external characteristics, such as origin, solubility, coagulability, and the like. On the basis of such properties, we distinguish to-day some forty to fifty natural proteins, discovered by the joint labours of chemists and physiologists; but it is to be expected that as the methods of differentiating and separating them are improved, their number will be largely increased.

At present the majority are known only in an amorphous form; some important terms of the group, however, such as oxyhæmoglobin, egg albumin, and the albumin of horse serum, excelsin from the Brazil nut and the edestins from other plant seeds, have been obtained in definite crystals. But, unfortunately, it cannot be decided from their crystalline appearance whether these products are definite substances, as the tendency to form mixed crystals is the greater the more complicated the molecule. Examples in point are afforded by the aniline dyes, the higher fatty acids, and the purine compounds; and those who have studied the chemistry of the natural silicates will be aware of the extension which mineralogists have been compelled to give to the conception of isomorphism. It would therefore be altogether surprising if the crystallised natural proteins should turn out to be single substances. In this gathering of expert chemists I need not dwell on the difficulties to which this uncertainty gives rise.

(To be continued).

NOTICES OF BOOKS.

Practical Test Book of Chemistry. By John Dabney Palmer, M.A., M.D. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1907.

This book contains an alphabetical arrangement of tests for the presence of various substances which the analytical chemist or pharmacist is likely to come across in the course of his work, and also tests for the purity of many foods and drugs. The methods have been collected from various sources, and have apparently not always been checked by the author himself, but have merely been copied from chemical and pharmaceutical journals. The various experiments appear to be described sufficiently fully as a rule, but in some cases a rearrangement of the order in which they are given would mean a possible saving of time for the experimenter, who will find no hints as to the relative sensitiveness or applicability of the tests. The examination of substances for purity is not well treated, and again the reader will look in vain for suggestions about the order in which he should apply the tests, so that he may in all cases search first for the most probable adulterants. As an instance of the author's method, we may call attention to the following case:—The analyst who had under his hand a sample of coffee for examination for purity would probably want to find quick and trustworthy methods of detecting the presence of common adulterants, and possibly estimating the amount of them present. When, however, he turned up "coffee" in the book he would find described only two experiments which would enable him to ascertain whether the sample contained any genuine coffee at all. Again, the methods given for examining butter are not sufficiently accurate or definite, and although they may be rapid and simple enough to show roughly whether the specimen examined contains large amounts of adulterant or not, they would probably be found quite inadequate to give any definite results in cases in which the adulteration had been skilfully carried out. The choice of substances in both parts of the book is purely arbitrary, and some omissions of important substances are by no means balanced by the details of the reactions of many rarer compounds which might possibly otherwise be found only by reference to original papers.

The Bacteriological Examination of Disinfectants. By William Partridge, F.I.C. London: The Sanitary Publishing Company, Ltd. 1907.

The greater part of this book is occupied with a complete description of the Rideal-Walker method of determining the germicidal value of a disinfectant. The author, owing to his familarity with the manipulation of the test, is in a position to give his readers many hints relating to details which may appear trivial, but which have, nevertheless, no little bearing upon the success of the method, and the neglect of which may lead to discrepancies. These small matters will receive the attention they deserve only from one who thoroughly realises that the bare outlines are not sufficient to enable the uninitiated to perform even comparatively simple tests in bacteriology, and they make all the difference to the practical usefulness of any book on the subject. The Preface is contributed by Major Fowler, R.A.M.C., who shortly discusses the question of the standardisation of disinfectants, and defends the Rideal-Walker method against those who criticise it owing to the apparently discrepant results which have been obtained when it is employed.

CORRESPONDENCE.

MELTING-POINTS.

To the Editor of the Chemical News.

Sir,—I shall be glad if any reader can inform me whether the melting-points are known of butane, pentane, and the higher members of the paraffin series up to octane, and, if so, where information on the subject can be found.

The melting-points of methane, ethane, and propane indicate that compounds containing an uneven number of carbon atoms are lower than those containing an even number, and it would be interesting to know whether this feature continues in the higher members of the series.—I am, &c.,

Ed. E. Price.

MISCELLANEOUS.

Direct Quantitative Separation of Chlorides and Bromides.—A correspondent points out that the equation on p. 183, vol. xcvi., of the Chemical News, in Mr. Andrews's article on this subject, should be—

$$2KH(IO_3)_2 + 20KBr + 11H_2SO_4 = 10Br_2 + 2I_2 + 12H_2O + 11K_2SO_4.$$

MEETINGS FOR THE WEEK.

Friday, 25th.—Physical, 5. "Use of Variable Mutual Inductances," by A. Campbell. "Magnetic Oscillators as Radiators in Wireless Telegraphy," by J. A. Fleming.

Tuesday, 29th.—Faraday Society, 8. "Electrolysis of Salt Solutions in Liquefied Sulphur Dioxide at Low Temperatures," by B. D. Steele. "Action of Aluminium Powder on Silica and Boric Anhydride," by F. E. Weston and H. R. Ellis. "Reduction of Metallic Oxides by means of Calcium Hydride," by F. M. Perkin and L. Pratt. Exhibition of a Series-parallel Lamp Resistance useful for Electro-chemical Work, by N. T. M. Wilsmore.

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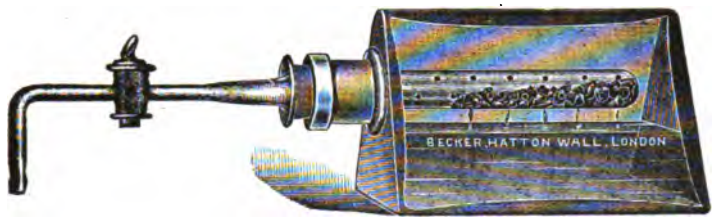

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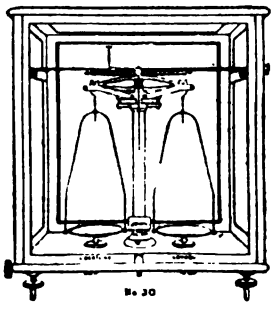

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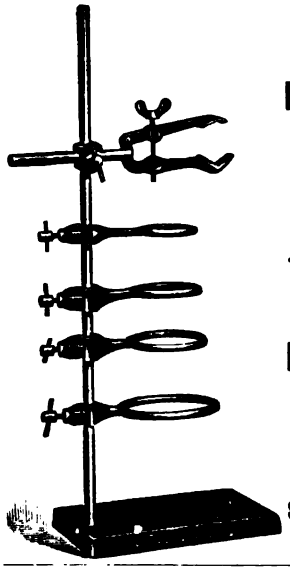

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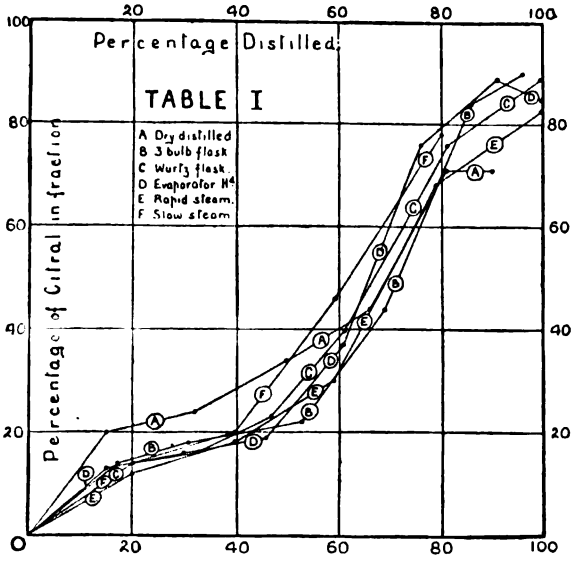
FRACTIONAL DISTILLATION BY MEANS OF STEAM.*

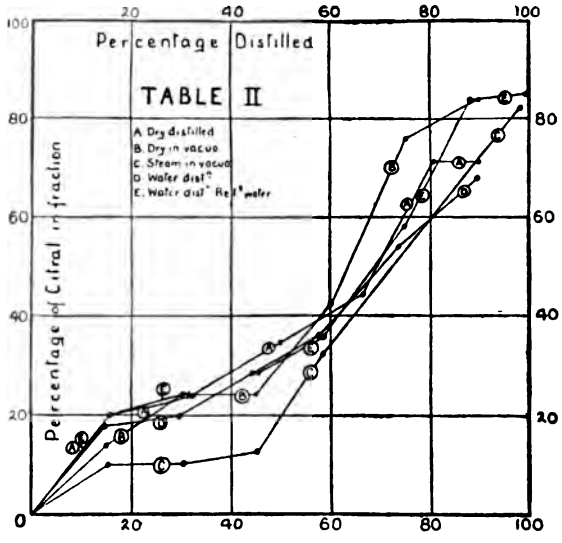
By HERBERT HARDY and BERNARD E. RICHENS.

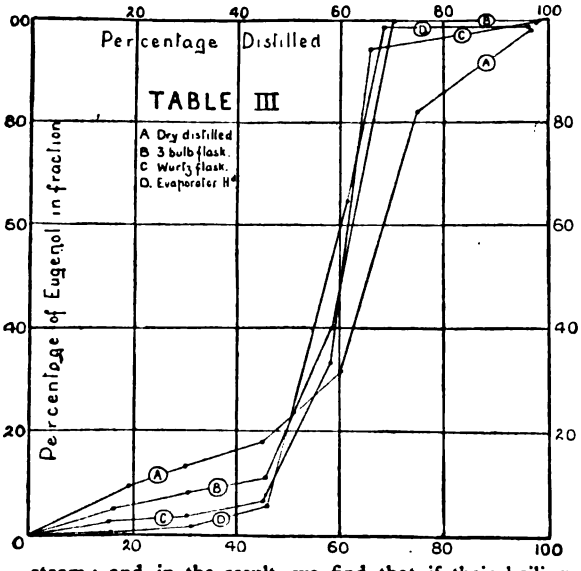
WE have experimented in regard to the degree of fractionation that may be obtained when two liquids that are immiscible with water are distilled in a current of live steam; and, in the result, we find that if their boiling-points are not too close together, they may be separated as well—and often better—by steam distillation as by ordinary ("dry") distillation.

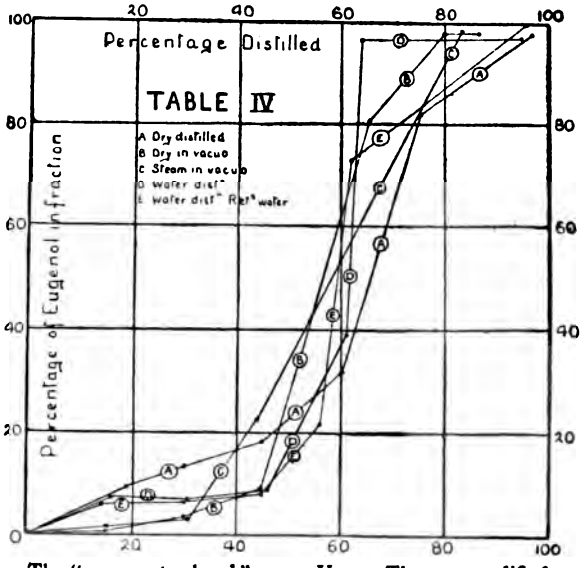
The accompanying tables apply to results obtained with mixtures of (*a*) limonene and citral (I. and II.) and (*b*) limonene and eugenol (III. and IV.) in equal volumes, and indicate the percentage of citral or eugenol in each fraction collected.

"Water distillation" means that the mixture of chemicals and water was distilled together from the same flask (in place of passing the steam from a separate boiler, as in the other cases), and "returning water" refers to a similar series of experiments where the aqueous portion of the distillate was returned to the distilling flask from time to time, so as to keep the volume of liquid in the flask nearly constant.









The "evaporator head" was a Young-Thomas modified evaporator head with three compartments.

The rate of distillation was normally 60 drops per minute of total distillate (water, &c.), but we also worked at 40 drops ("slow steam") and 180 drops ("rapid steam") per minute.

* Abstract of a Paper read before the Society of Public Analysts, December 5, 1906. The original appeared in the *Analyst* for June, 1907, and we are indebted to the Editor of that journal for the loan of the blocks illustrating this article.

As may be seen from the curves, the general results are —(*a*) That distillation by means of steam gives *at least* as good a fractionation as ordinary dry distillation; (*b*) that steam under reduced pressure is specially efficient; (*c*) that the use of a fractionating column has but little effect; and (*d*) that the results are but slightly influenced by the rate of distillation, the more rapid being rather better.

The method applies only to substances insoluble in water.

Limonene and cineol have both b. p. 176° C. and citral 228—230°.

RED SEA WATER.

By JOHN B. COPPOCK, B.Sc. (Lond.), F.I.C., F.C.S.

DURING September of this year a sample of Red Sea water, from Port Soudan, came into my hands for analysis. No analysis of this sea water seems to have been recorded, hence it was thought desirable to publish the following figures.

The analysis is of the usual type as far as the inorganic constituents of sea-water are concerned, but differs from the usual type by the determination of the constituents usually in water analysis grouped under the heading "free and albumenoid ammonia." These latter substances were determined by a modification of the American official alkaline permanganate method for nitrogen availability in tankage, sodium nitrate, &c., and which has been shown to give satisfactory results.

Analytical Figures.

		Per cent.
Total solids—		
Amount obtained by evaporation at 100° C.		4·84
Amount obtained when dried in steam-oven and finished in desiccator		4·34
Inorganic substances—		
Chlorine	2·09	
Sodium	1·18	
Magnesium	0·135	
Calcium	0·052	
Sulphates (SO_4)	0·206	
Carbonates (CO_3)	0·007	
	3·670	
Other constituents and water of crystallisation	1·170	
		4·840
Ammonia determinations—		
Free ammonia		0·00014
Calculated as NH_4Cl		0·00043
Albumenoid ammonia		0·00042
Calculated as albumenoids		0·00222

The free ammonia represents that which came off on distillation with a small quantity of sodium carbonate; the albumenoid ammonia that which came off on treatment of the water with 15 grms. of caustic soda and 1·6 grms. of potassium permanganate.

Specific gravity at 10° C., 1·027.

Chemical Laboratory, Kendal.

Action of Alkalis on Tetrathionates.—A. Gutmann.—When about 15 per cent alkali solution, NaOH, KOH, $Ca(OH)_2$, $Ba(OH)_2$, acts upon a tetrathionate sulphite and thiosulphate are formed: $2S_4O_5 = 3S_2O_2 + 2SO_2$ or $2S_4O_6Na_2 + 6NaOH = 3S_2O_3Na_2 + 2SO_3Na_2 + 3H_2O$. If concentrated alkali solution (1 : 1) is used some sulphide is obtained in addition, the reaction being $3S_4O_5 + H_2O = 3S_2O_2 + 5SO_2 + H_2S$ or $3S_4O_6Na_2 + 12NaOH = 3S_2O_3Na_2 + 5SO_3Na_2 + Na_2S + 6H_2O$. No sulphate was formed in the author's experiments.—*Berichte*, xl., No. 13.

SYNTHETICAL CHEMISTRY IN ITS RELATION TO BIOLOGY.*

By Prof. EMIL FISCHER, F.R.S.

(Concluded from p. 210).

OF the numerous attempts to unravel the constitution of the proteins by analytical means, the only method which has given useful results hitherto is that of hydrolysis. Hydrolysis can be effected by acids or by alkalis, and also by digestive enzymes; the products, it is well known, besides ammonia, are albumoses, peptones, and ultimately amino-acids. The wide range of variation in composition of these amino-acids is illustrated in the following list:—

Glycine (Braconnot, 1820).
Alanine (Schützenberger, Weyl, 1888).
Valine (v. Gorup-Besanez, 1856).
Leucine (Proust, 1818; Braconnot, 1820).
*iso*Leucine (F. Ehrlich, 1903).
Phenylalanine (E. Schulze and Barbieri, 1881).
Serine (Cramer, 1865).
Tyrosine (Liebig, 1846).
Aspartic acid (Plisson, 1827).
Glutamic acid (Ritthausen, 1866).
Proline (E. Fischer, 1901).
Oxyproline (E. Fischer, 1902).
Ornithine (M. Jaffé, 1877).
Lysine (E. Drechsel, 1889).
Arginine (E. Schulz and E. Steiger, 1886).
Histidine (A. Kossel, 1896).
Tryptophane (Hopkins and Cole, 1901).
Diaminotrihydroxydodecanoic acid (E. Fischer and E. Abderhalden, Skraup, 1904).
Cystine (Wollaston, 1810; K. A. H. Mörner, 1899).

In this list are included all the substances hitherto prepared from the proteins the existence of which is established, with a short reference to their discovery. It may, however, be mentioned that the list is by no means complete; among the new products already announced, the caseanic acid described by Skraup appears to have the greatest claim to recognition as a definite substance. It is certain, however, that the nineteen amino-acids in the list are the chief hydrolytic cleavage products of the proteins and those which are most generally met with. Their discovery has been made during a period of eighty-four years, but no less than five of them have been recognised within the new century.

The proportions in which the various amino-acids are obtained from the different proteins vary very considerably. In some cases they are altogether lacking, as may be proved by application of the definite tests for tyrosine, tryptophane, or glycine; but it is worthy of note that, as a rule, the amino-acids referred to as isolated from the mixtures produced by subjecting albuminous substances to hydrolysis all occur almost without exception, especially is this true of the important proteins which play the chief part in animal or vegetable metabolism, so that the conclusion must be drawn that none of them can be dispensed with in organic life. With the exception of diaminotrihydroxydodecanoic acid, they have all been so thoroughly investigated that their structure is well established. The majority also have been synthesised, proof of their structure having, in fact, been given in this way. Only oxyproline, histidine, and diaminotrihydroxydodecanoic acid remain still to be synthesised.

With the exception of glycine, all the amino-acids derived from natural sources are optically active; but when prepared by ordinary synthetic methods, as is well known, they are obtained in the first instance in the racemic form. The resolution of the racemoids into their optically active

* Faraday Lecture, delivered before the Chemical Society, October 18, 1907. From the *Transactions of the Chemical Society*, 1907, vol. xci.

components has been effected quite recently in most cases. Asparagine, however, which is closely related to aspartic acid, has been resolved into the two active forms by recrystallising the inactive synthetic product from water, and separating the two constituents mechanically. Moreover, in the case of some other amino-acids, for example, leucine, the antipode of the natural form had been obtained by partially fermenting the synthetic product with moulds. The complete synthesis of the active amino-acids which are obtained from natural sources was first accomplished by the method I introduced based upon the use of the acyl derivatives. The method has been applied with success to the majority of the synthetic products; its extension to the remaining cases, proline, lysine, tryptophane, and cystine, is not likely to be attended with any difficulties. The synthetical results are summarised in the following list, in which the inactive products are marked *dl* and the natural active products are recorded separately:—

Glycine (Perkin and Duppa, 1858).
Alanine *dl*- (A. Strecker, 1850).
Alanine *d*- (E. Fischer, 1899).
Valine *dl*- (Fittig and Clark, 1866).
Valine *d*- (Fischer, 1906).
Leucine *dl*- (Limpricht, 1855; E. Schulze and Likiernik, 1885).
Leucine *l*- (Fischer, 1900).
*iso*Leucine *dl*- (Bouveault and Loquin, 1905).
*iso*Leucine *d*- (Loquin, 1907).
Phenylalanine *dl*- (Erlenmeyer and Lipp, 1883).
Phenylalanine *l*- (Fischer and Schöller, 1907).
Serine *dl*- (Fischer and Leuchs, 1902).
Serine *l*- (Fischer and Jacobs, 1906).
Tyrosine *dl*- (Erlenmeyer and Lipp, 1883).
Tyrosine *l*- (Fischer, 1900)
Aspartic acid *dl*- (Dessaignes, 1850).
Aspartic acid *l*- (Piutti, 1887).
Glutamic acid *dl* (L. Wolff, 1890).
Glutamic acid *d*- (Fischer, 1899).
Proline *dl*- (R. Willstätter, 1900).
Ornithine *dl*- (Fischer, 1900).
Ornithine *d*- (Sörensen, 1905).
Arginine, active; partial synthesis from ornithine (E. Schulze and Winterstein, 1899).
Lysine *dl*- (Fischer and Weigert, 1902).
Tryptophane *dl*- (A. Ellinger and Flamand, 1907).
Cystine *dl*- (Erlenmeyer, jun., 1903).

I have been able to refer the configuration of some of these substances to that of glucose. This correlation was first effected thirteen years ago in the case of aspartic acid. As you are aware, this acid is converted by nitrous acid into *l*-malic acid, the configuration of which can be deduced from its relationship to tartaric acid. In a similar manner, it has been found possible recently to connect serine and alanine with active glyceric acid, which Neuberg and Silbermann have been able to correlate with tartaric acid, and which it may be anticipated will also be obtained directly from the tetroses by adopting methods such as those introduced by Wohl and Ruff. It will probably be found that the method is applicable to most of the other amino-acids, so that it is to be expected that at no distant date a uniform steric system will be established which will include all the optically active substances in the sugar group, the hydroxy-acids, and the amino-acids.

It is not without purpose that I have dwelt so long on what appear to be side issues of synthetic work, for I firmly believe that they will prove in many respects to be of service to biological inquiry. In proof of this, reference may be made to several cases in which they have already borne fruit. For example, the proof given by E. Schulze and Winterstein that arginine is a derivative of guanidine, and therefore also of urea, had undoubtedly some influence in stimulating H. Kossel to the discovery of the interesting manner in which this amino-acid is resolved into urea and ornithine by means of liver arginase.

To test the assumption that ornithine and lysine are carboxylic acids of tetra- and penta-methylenediamines, Ellinger subjected these substances to the action of putrefactive bacteria, and was successful in converting them into the well-known basic products of putrefaction.

The manner in which taurine is formed in the animal body has been made clear by Friedmann's proof of the relation between cystine and taurine.

The isolation of tryptophane by Hopkins and Cole, and its conversion into scatole, enable us to form a clear picture of the manner in which this offensive substance is produced by intestinal putrefaction, and to indicate also the origin of the indoxylsulphuric acid discovered by E. Baumann in urine, and of the indigo-blue which is sometimes met with in this secretion. I need do no more than point out, however, that this connection could not possibly have been established had not A. von Baeyer laid the foundation by his great synthetic achievements in the indigo group.

The discovery of *iso*leucine and its relationship to leucine led F. Ehrlich, a few years ago, to undertake his interesting experiments on the conversion of amino-acids into primary alcohols by means of beer yeast, which enabled him to give the long-sought explanation of the formation of fusel oil during alcoholic fermentation.

Such instances will be multiplied rapidly in the future; considerations of the relationship of the natural amino-acids to various other classes of substance from the structural and stereo-chemical point of view are formulated so easily and in such a variety of directions that they can afford much fruitful stimulus to physiological inquiry.

As the amino-acids are formed from the proteins, not only when these are subjected to the action of hot acids and alkalis but also at moderate temperatures by the agency of the digestive enzymes, they are to be regarded as the true foundation stones of protein molecules. Opinions adverse to this hypothesis are only occasionally met with; they centre round the arbitrary supposition that complicated atomic re-arrangements may take place during hydrolysis.

Were one inclined to regard such objections as of moment, all the experiments on the determination of the constitution of organic compounds by degradation methods would be useless; moreover, the conclusions which have been drawn in other cases from the results obtained by the dissection of compounds have been too frequently confirmed by their synthesis. It is now possible to make this claim on behalf of the proteins, as it has been found to be possible, by a process the reverse of hydrolysis, to associate amino-acids in such a manner that substances are produced which, in the case of the simpler terms, closely resemble peptones, whilst the more complex resemble proteins.

I have termed these synthetic products *polypeptides*, in view of their relationship to the peptones and to facilitate systematic treatment of the group on the lines of the carbohydrates.

No useful purpose will be served by my giving an account of the synthetical methods on the present occasion, especially as I had the honour, six months ago, of describing to you the preparation of an octadecapeptide derived from 15 molecules of glycine and 3 molecules of *l*-leucine, a substance which in its external properties closely resembles many natural proteins. I may say that more than one hundred of these artificial polypeptides have already been synthesised.

Many of them, it is true, belong to the lower stages, but all the amino-acids previously mentioned, with the exception of diaminotrihydroxydodecanoic acid, have been made use of in their preparation. The synthesis of the higher terms has been restricted hitherto to the combinations of glycine, alanine, and leucine; there is not a shadow of doubt, however, that all the remaining amino-acids could be associated in complicated systems with the aid of our present methods. The knowledge of the artificial polypeptides thus acquired has opened up new ways of investigating the peptones and albumoses analytically. During

more than fifty years, physiological chemists have endeavoured without much success to isolate homogeneous substances from these ill-defined materials; all the products described by them, however, bear indubitable evidence of being mixtures. By making use of new methods based on the study of the polypeptides, it has been possible during the last two years to isolate and detect with certainty quite a number of dipeptides among the decomposition products of the proteins. In conjunction with Abderhalden, I have succeeded in separating glycyl-*d*-alanine, *d*-alanyl-*l*-leucine, and *l*-leucyl-*d*-glutamic acid from silk fibroin, elastin, and gliadin respectively. We have definitely proved the existence of dipeptides of glycine with *l*-leucine and *l*-tyrosine in the form of anhydrides, and our work has made it probable that other combinations exist; for example, that of glycine with valine. P. A. Levene has discovered glycyl-proline anhydride among the products of the digestion of gelatin, whilst T. B. Osborne and S. H. Clapp have noted a dipeptide derived from phenyl-alanine and proline among the products of the hydrolysis of gliadin by hot sulphuric acid. A tetrapeptide of fairly definite composition has been isolated by Abderhalden and myself from silk fibroin, and, although its homogeneity is not yet quite established, it is certainly in great part a combination derived from two glycine molecules with one of *d*-alanine and one of *l*-tyrosine. The substance is of special interest on account of its close resemblance to the albumoses. Moreover, *l*-leucyl-triglycyl-*l*-tyrosine prepared artificially has all the properties of the albumoses. These observations are of importance as casting doubt on the view which formerly prevailed that, being intermediate products between proteins and peptones, the albumoses are substances of considerable molecular complexity.

This may be true of many of the substances hitherto described under the name, all of which are certainly mixtures; but it is clear that many others are no more complex than the albumose above referred to from silk or the artificial pentapeptide.

In spite of these encouraging successes, I am fully aware of the difficulty of discovering the nature of all the components of the various peptones and albumoses. But in preparing the way for the synthesis of the natural proteins this is not even necessary. Probably the work can be restricted to the re-construction of the original system from the major products of cleavage formed in the process of hydrolytic dissection. I am, indeed, venturesome enough to cherish the hope that I may he able to solve this problem in the case of silk fibroin, one of the simplest proteins. To deal with the whole of the proteins will be a gigantic task; so large a number of separate investigations will be necessary that nothing less than the life-work of a whole army of inventive and diligent chemists will suffice to complete it. Probably, too, the unpleasant discovery will be made that the natural proteins as we know them to-day are only to be obtained by mixing the homogeneous artificial products.

I have sketched this prospect merely to indicate the manner in which synthesis must play the leading part in this field of work. The nature of the more complicated carbohydrates, as I have already pointed out, will also have to be determined in the future, I imagine, mainly by the application of synthetic methods. Obviously the conditions are very similar in the case of the dextrins and gums to those met with in the case of the proteins, and starch, which has hitherto been regarded as a homogeneous substance, appears also to come into the same category, according to Maquenne's observations.

Not only do the proteins constitute the major part of living protoplasm, but they appear also to be the material from which the organism prepares its most wonderful agents; the ferments or enzymes. In many of the more thoroughly investigated biological processes their co-operation has been demonstrated, and there is good reason to suppose that they take part in all changes occurring within the living cell. So much is certain, the physiological chemistry of the future will be largely concerned with the study of fermentative changes; many indications that this must be the case are to be met with in tracing its latest developments.

The number of the enzymes has been increased to an extraordinary extent during the last ten years. I may allude to the newly-discovered enzymes correlated with the carbohydrates, maltase, lactase, mellibase, trehalase, amygdalase, inulase; to the various oxidases, laccase, tyrosinase; to the lipases, erepsin, enterokinase, arginase, the sucroclastic and glucosidoclastic enzymes, and finally to the zymase of alcoholic fermentation. Much valuable information has been accumulated as to the manner in which they act, as to their formation from zymogens, and as to their assistance by co-ferments and their retardation by chemical agents or by antiferments. The specific character of their action, in other words, their dependence on the structure and configuration of the object they attack, has been proved beyond doubt, and favours very definitely the assumption that enzyme and hydrolyte enter temporarily into combination, a conclusion to which H. E. Armstrong and E. F. Armstrong have quite recently again very properly drawn special attention. But, unfortunately, we know practically nothing of the composition of the enzymes, as the complete isolation of an enzyme has never been accomplished.

From observations hitherto made, it appears in a measure probable that they are derived from proteins, and possess a protein-like character. If this be so, it may be hoped that the experience gained with the proteins will be of service in the investigation of enzymes.

In the meantime there are other directions in which synthetic chemistry can be of service in elucidating the chemistry of fermentation. In the same way that the artificial glucosides have been of use in establishing the dependence of the action of enzymes on configuration, the synthesised polypeptides are now being used by Abderhalden, Euler, and others to define and measure the activity of the proteoclasts. In a like manner, the synthetic exploration of the purine group has served to direct the recent observations on the fermentative de-amination and oxidation of adenine, guanine, and xanthine. Finally, attention may be directed to the use that has been made of stereochemical considerations in the course of Bertrand's interesting studies of the oxidation of polyhydric alcohols by the sorbose bacterium.

Not only have the methods of organic chemistry proved to be fruitful of results in the case of the proteins but also when applied to complex derivatives of the latter, such as the nucleo-proteins, for example. Thus we are indebted to the brilliant researches of A. Kossel and his school for our knowledge of no less than four bases of the pyrimide and purine group obtained by breaking down nucleic acids, and the analytical investigation of the latter has already been carried so far that, in the opinion of H. Steudel, it is to be expected that their synthesis will be effected at no distant date. Similar success may be hoped for even sooner in the case of the lecithins. Structural chemistry, moreover, is slowly acquiring the mastery over cholesterin by making use of the experience afforded by the synthetic study of the hydroaromatic substances.

Besides the old well-known constituents of the animal body, new substances having quite unexpected properties have been added from time to time. Such are iodothyrin from the thyroid gland—discovered by Baumann—and crystalline adrenaline—isolated by Takamine from the supra-renal capsule—minute doses of which increase the blood-pressure. Judging from analytical results and the synthesis effected by F. Stolz, adrenaline possesses a relatively simple structure. In the opinion of the discoverers, this is probably true of the "pancreatic secretin" made known by Bayliss and Starling's researches, which has the remarkable property of liberating enzymes from the pancreas. May it not also be true of the toxins of many infectious diseases and of the antitoxins used in serum therapeutics, the discovery and systematic investigation of

which by Behring, Roux, P. Ehrlich, and others are to be reckoned among the greatest achievements of modern biology and medicine?

The methods of organic synthesis will certainly serve to throw light on the nature of all such substances of animal origin. Equally numerous problems await solution in the plant world.

The great success with which the alkaloids and terpenes have been studied during the past ten years is known to all, but it is only too obvious that much still remains to be done when such substances as quinine, morphine, and caoutchouc remain to be synthesised.

Alizarin and indigo are prepared artificially in huge quantities, and we are well informed as to the structure of hæmatoxylin and kindred substances; but our ignorance is correspondingly great of most of the blood colouring matters as well as of many coloured constituents of our own bodies: of the air, the skin, and the eye.

The fullest recognition must be accorded, however, to recent investigations on the complex colouring matters of the blood and of chlorophyll, which is distantly related to the former, associated with the names of Schunck, Nencki, Marchlewski, Küster, and Willstätter.

In fine, the aid of synthetical chemistry is required in every direction in arriving at a clear understanding of structure and of change. The methods at our disposal in the laboratory are doubtless altogether different from those which come into operation in the living world, but chemists are already trying to effect changes in carbon compounds by means of so-called mild interactions, under conditions comparable with those which prevail in the living organism. It may suffice to refer to the development of a number of catalytic processes, and to the comprehensive studies on the action of light on organic substances undertaken by Ciamician. In fact, the effort is already being made to co-operate with biology; it is clear that a section of the forces of organic chemistry are being directed once more towards the goal from which it set out. The separation from biology was necessary during the past century while experimental methods and theories were being elaborated; now that our science is provided with a powerful armoury of analytical and synthetical weapons, chemists can once more renew the alliance both to its own honour and to the advantage of biology. Indeed, the prospect of obtaining a clearer insight into the wondrous series of processes which constitute animal and vegetable life may well lead the two sciences to work with definite purpose to a common end.

In order, as far as possible, to avoid mistakes in this difficult task, and to shield ourselves from the disappointment which is the inevitable consequence of exaggerated hopes, we cannot do better than strive to imitate the great example of Faraday, who always with rare acumen, directed his attention to actual phenomena without allowing himself to be influenced by preconceived opinion, and who in his theoretical conceptions gave expression only to observed facts.

Dennstedt's Simplified Combustion Method.—R. Baumert.—The author finds that in Dennstedt's method substances which generate gases which burn with difficulty often fail to undergo complete combustion. The following modification of the method is rather simpler and more satisfactory. The same furnace is used, but the tubes have the ordinary combustion tubing diameter of 18 mm., and the boats, &c., are smaller in proportion. Instead of platinum quartz copper oxide asbestos is used for substances which do not contain halogens and platinum asbestos for those which do. Silver asbestos is used instead of molecular silver, and lead peroxide asbestos instead of lead peroxide. The absorption apparatus is the same as Prof. Dennstedt's.—*Berichte*, 1907, xl., No. 13.

THE MOLECULAR WEIGHT OF ARGENTIC SULPHATE, AND THE ATOMIC WEIGHT OF SULPHUR.*

By THEODORE WM. RICHARDS and GRINNELL JONES.

(Concluded from p. 205).

The Conversion of Argentic Sulphate into Chloride.

THE next step in the process was the conversion of the carefully weighed fused sulphate into chloride by heating it in a current of dry hydrochloric acid gas. This reaction has been observed by Hensgen (*Recueil des Travaux Chimiques de Pays-Bas.*, 1883, ii., 124):—

"Le sulfate d'argent absorba 2 mol. HCl à la température ordinaire, avec un dégagement de chaleur notable, et se changea complètement en chlorure. En chauffaut, même jusqu'a 300°, la réaction inverse (observée par M. H. avec le sulfate de cuivre) n'eut point lieu, mais l'acide sulphurique fut chassé complètement par un courant d'air. Parmi les sels susdits, le sulfate d'argent est celui qui d'après les données thermiques doit se changer en chlorure avec le plus grand dégagement de chaleur." (See below).

The hydrochloric acid generator used for the previous work was constructed entirely out of glass. Pure ammonic chloride or concentrated hydrochloric acid was placed in the flask (I) shown in Fig. 4, and concentrated sulphuric acid was dropped upon it slowly. The gas was dried by passing through the tower (J) containing beads moistened with concentrated sulphuric acid (see Note). The gas then passed through the stopcock (K) to the delivery tube (N). The ground-glass stopper at the top of the tower (J) acted as a safety-valve when the stopcock (K) was closed. Pure dry air might also be delivered at N by means of the stopcock (L), in order to sweep out the excess of acid at the conclusion of the reaction.

(NOTE.—In one of the preliminary experiments the hydrochloric acid was not dried. The sulphuric acid first formed absorbed considerable water, thus becoming diluted and nearly filling the tube with liquid sulphuric acid in which a large part of the silver sulphate dissolved. After heating for some time, the whole mass was solidified. This gave a non-porous mixture of silver sulphate and chloride. The hydrochloric acid had no appreciable further action until the mixture was fused, and then the action became very vigorous. The sulphuric acid which was formed boiled, and caused spattering, and therefore danger of mechanical loss).

The quartz tube containing the argentic sulphate was supported by means of hooks of hard glass in front of the delivery tube (N), as before, without making a tight joint.

In seven of the final experiments a condenser tube of quartz (O) was placed over the exit end of the tube (M) in order to condense the sulphuric acid and retain any silver which might escape. As will be shown, only very small traces of silver were found in the distillate. The condensation of sulphuric acid in the narrow tubes on the end was prevented by keeping them hot by means of a small fixed fish-tail burner.

A slow current of hydrochloric acid was generated, and the tube warmed gently. The reaction took place readily and quietly, the only difficulty being that the argentic chloride formed was inclined to creep over the walls of the vessel. This was probably due to the liberated sulphuric acid having dissolved undecomposed argentic sulphate; the acid sulphate was then transported by surface tension, and converted into chloride in another place. In two of the experiments one of the narrow end tubes was completely blocked up in this manner, making a successful completion of the experiment impossible, but in other cases the difficulty was avoided by starting with the argentic sulplate in a band in the middle of the tube.

The sulphuric acid must be evaporated at a temperature below its boiling-point in order to avoid loss by the pro-

* *Publication* No. 69, Carnegie Institution of Washington.

jection of small particles. The tube was heated by a flame held in the hand, the heating being regulated by watching the escaping fumes of acid and also the colour of the argentic chloride in the tube. It is well known that as the temperature increases, silver chloride acquires a deeper and deeper yellow colour, and after acquiring the necessary experience, this change of colour proved very helpful in egulating the temperature.

After from 2·5 to four hours no more fumes of sulphuric acid could be seen issuing from the tube. The argentic chloride was then fused very slowly and quietly, and kept in the fused state for twenty minutes in a current of hydrochloric acid. The tube was gently agitated in order to expose a fresh surface, at intervals of about one minute, by grasping the exit end with platinum forceps. The agitation can be performed without danger of loss, because of the high surface tension of fused argentic chloride. This material when liquefied does not adhere to quartz, and therefore is not drawn into the end tubes by capillarity. At the expiration of twenty minutes the current of acid gas was stopped by means of the stopcock (K), and a current of pure dry air was passed through the tube through L, the argentic chloride being still maintained in the liquid state for at least five minutes with occasional agitation. The tube was rotated while subsequently cooling in a similar manner to that employed with the sulphate.

The condensed sulphuric acid evolved by the reaction and the condenser tube were tested for silver by means of the nephelometer (Richards and Wells, *Am. Chem. Journ.*, 1904, xxxi., 235). The acid was transferred to a small flask, and the tube was rinsed with ammonia, which was added to the acid. The excess of ammonia was then neutralised with nitric acid, and hydrochloric acid was added to precipitate any trace of silver present as an opalescent cloud of argentic chloride. This opalescence was compared in the nephelometer with a standard which had been made in a manner very similar to the unknown solution (Richards, *Am. Chem. Journ.*, 1906, xxxv., 510). A measured volume of a standard silver solution was taken; to it were added approximately the same amounts of sulphuric acid, ammonia, and nitric and hydrochloric acids as were present in the unknown solution, and it was made up to the same volume (about 30 millilitres).

The greatest amount of argentic chloride thus found in any experiment was 0·00009 grm., and the average amount 0·00004 grm. The trace found in this way was of course added to the weight of the silver chloride. In three of the experiments (Nos. 4, 5, and 7) this determination was not made, but the average amount is added in these cases. The probable reason for the escape of this trace of silver will be discussed later.

The question as to whether or not this reaction is complete is, of course, of fundamental importance. There are four pieces of evidence bearing on this point,

In the first place, the argentic chloride was fused for twenty minutes in a current of almost pure hydrochloric acid. Since the temperature was far above the boiling-point of sulphuric acid, this product of the reaction was driven off as fast as formed. Therefore, according to the law of concentration-effect it is to be expected that, through the agency of the continually renewed hydrochloric acid, all the argentic sulphate would be decomposed, and all the sulphuric acid would be driven off. This would be hastened by the fact that fresh surfaces were continually exposed through agitation.

Again, in this case the law of concentration-effect is assisted by the relative affinity, indicated approximately by the large amount of heat evolved by the reaction. It can be calculated from Thomsen's data that the reaction gives out 40,400 grm.-calories, or 170 kilojoules (see Note). Rarely, if ever, is the difference between total-energy and free-energy changes in a reaction of this kind as great as this, hence it is safe to infer that there is a considerable preponderance of driving tendency in the desired direction, arising from the mutual affinities concerned.

Note. — Thomsen, "Thermochemische Untersuchungen":—

$2Ag + Cl_2 = 2AgCl + 58760$ (vol. iii., p. 381).

$Ag_2SO_4 = 2Ag + O_2 + SO_2 - 96200$ (vol. iii., p. 382).

$SO_2 + O_2 + H_2 = H_2SO_4 + 121840$ (vol. ii., p. 255).

$2HCl = H_2 + Cl_2 - 44000$ (vol. ii., p. 114).

Therefore, $Ag_2SO_4 + 2HCl$ (gaseous) $= 2AgCl + H_2SO_4$ (liquid) $+ 40400$.

A different set of equations gave 40,200. The result, of course, only applies to 18°. In this connection it is worth while to note that $Ag_2SO_4 + Cl_2 = 2AgCl + SO_2 + O_2 - 37440$ cals.; which indicates that chlorine would not be as suitable for our purpose as hydrochloric acid. This expectation is confirmed by the experience of Krutwig (*Ber.*, 1881, xiv., 306): —"Die Einwirkung ist hier (chlorine on silver sulphate) keine direkte; nur bei sehr hoher Temperatur, nachdem das Salz geschmolzen ist und sich zersetz, giebt es schweflige Saüre, Chlorsilber, und Sauerstoff ab."

Thirdly, constancy of the weight on continued treatment indicated the completion of the reaction. In seven of the experiments the argentic chloride was fused a second time in hydrochloric acid for fifteen minutes with occasional agitation, followed by five minutes in air. The following table gives the changes in weight found in this way:—

The Effect of Continued Treatment with Hydrochloric Acid.

No. of experiment	AgCl, first weighing.	AgCl, second weighing.	Difference.
6.	4·67812	4·67809	−0·00003
7.	4·93119	4·93118	−0·00001
11.	4·67373	4·67375	+0·00002
13.	4·74491	4·74489	−0·00002
14.	4·77995	4·77990	−0·00005
15.	4·94088	4·94088	0·00000
		Average	−0·000015

The constancy in weight was thus entirely satisfactory, the average loss being only 0·0003 per cent of the weight of the chloride.

This experiment, however, does not absolutely preclude the possibility that a small but constant amount of sulphate may remain. In order to test this question, 4·90 grms. of argentic chloride which had never been contaminated with sulphate was fused in the tube, and then 0·00479 grm. of pure argentic sulphate was added and thoroughly mixed with the chloride by fusion. On cooling, the appearance was very different from the pure chloride, the mass being translucent or almost opaque instead of transparent. It was then fused in a current of hydrochloric acid for twenty minutes after the sulphuric acid could no longer be seen escaping from the tube, as before. On the assumption that the sulphate was converted completely into chloride the loss in weight would have been 0·00039 grm., while the actual loss in weight was 0·00044 grm. The reaction was evidently complete, and a fourth argument was added to the other reasons for believing that the process should yield satisfactory results.

It will be recalled that the narrow end tubes were kept very hot by small stationary burners in order to prevent the condensation of sulphuric acid. At the close of several of the experiments a very slight sublimate was observed on the portion of the narrow tubes which was kept somewhat cooler by the protection of the supporting hooks. This sublimate, although never large in amount, appeared largest in Experiments 6 and 10. There was a smaller amount in Experiments 7, 11, and 14, but none worthy of consideration in Experiments 4, 5, 12, 13, and 15. In Experiments 10 and 14 a slight amount of the sublimate was visible in the condenser also, near the end of the tube.

Although the most rational explanation of this trace of sublimate, which was usually too slight to be weighable, was probably to be found in the assumption that it was argentic chloride, and therefore entirely without sinister meaning except as suggesting the risk of the loss of other traces, the matter was studied further. Careful tests for

arsenic and copper were made with negative results, and the hydrochloric acid was demonstrated to contain no trace of anything which could be deposited in a red-hot quartz tube. (The test for arsenic was kindly made by Mr. O. F. Black). On the other hand, the sublimate was soluble in ammonia, and behaved in every way like argentic chloride, so that its nature was considered as nearly proved as was possible with such a minute amount of material. Having settled the nature of the sublimate, its source and significance must be traced. Evidently it could not have come from the main body of the silver sulphate, because it appeared at the very beginning of the experiment, as soon as the current of hydrochloric acid was started and the end tubes heated, before the heat was applied to the main body of the argentic sulphate. Moreover, the mass of the argentic chloride was never heated to a temperature high enough to volatilise weighable amounts of this substance, as was shown by the constancy of weight on continued heating in a current of gas. (See the preceding description; also Richards and Wells, *loc. cit.*, p. 60; Baxter, *Proc. Amer. Acad.*, 1905, xli., 83).

In view of these considerations, it seemed probable that a few invisible crystals of argentic sulphate had been left in the end tubes by the feather used in cleaning it, or carried into the end tube by the current of sulphur trioxide before fusion. As soon as the hydrochloric acid was admitted and the end tubes heated, these small invisible crystals of silver sulphate must have been at once converted into chloride, and sublimed to the cooler portion of the tube—for the end tubes were usually raised to a red heat. This explanation is consistent with the frequent absence of any significant sublimate, especially in the case of Experiment 15. In this experiment the tube had been dusted and treated with particular care, in order to test the point.

Because the sublimate was weighed in the tube which had previously contained the sulphate, its presence could not affect the accuracy of the results, even if it had been weighable. Nevertheless, the suggestion that another portion might have been carried out of the tube was worth considering. Doubts on this point were set at rest by the analysis of the contents of the condenser tube which received the volatile products of the reaction. The average amount of silver found in this tube was less than 0·001 per cent of that taken in each experiment, and the small appropriate correction was easily applied.

Although it was not probable that argentic chloride which had been fused in air for five minutes still retained any dissolved hydrochloric acid, this point also was tested. In Experiment 13, the silver chloride after the first heating in hydrochloric acid and fusion in air for five minutes as usual, weighed 4·74491 grms. After the second fusion in hydrochloric acid, and finally in air, the weight was 4·74489 grms. After another fusion for twenty minutes in a current of pure air, the weight was 4·74493 grms. These slight changes in weight can only be ascribed to errors in the weighing; the outcome shows that the argentic chloride after the usual treatment did not retain any dissolved hydrochloric acid. Richards and Wells (*loc. cit.*) have already shown that it does not dissolve weighable amounts of air.

In still another case the outside of the tube was washed with water to make sure that nothing had deposited on it during the long exposure to the flame and acid. The loss in weight was only 0·02 mgrm., which again is not greater than the possible error in weighing.

The Final Results.

Having shown the feasibility of the plan of operations and gained practice by three preliminary experiments, a final series was undertaken, whose outcome is detailed below.

Sample A of argentic sulphate was used in Experiments 4 and 5, and Sample B in the remainder. In Experiments 5 and 6 the hydrochloric acid was generated from ammonic chloride, and in the other experiments from concentrated hydrochloric acid. The corrected weight of argentic chloride was obtained by adding the trace found in the condenser to the average weight after fusion in hydrochloric acid. In Experiments 4, 5, and 7 the correction for the argentic chloride in the condenser was not determined directly, but the mean of the other determinations (0·00004 grm.) was added.

In Experiments 8 and 9 the narrow exit tube became completely blocked by the creeping of the argentic chloride. This made it necessary to fuse the solid while there was still present considerable argentic sulphate; and therefore the sulphuric acid boiled and material was lost by being projected out of the tube. The first of these was rejected and the second not finished. All the other determinations are recorded in full in the table. The weighings have of course been corrected to the vacuum standard.

The Quantitative Conversion of Argentic Sulphate to Chloride.

No. of experiment.	Weight of colourless Ag_2SO_4 in vacuum.	Weight of total AgCl in vacuum.	Parts of AgCl obtained from 100·000 parts of Ag_2SO_4.
4.	5·21962	4·79859	91·934
5.	5·27924	4·85330	91·932
6.	5·08853	4·67810	91·934
7.	5·36381	4·93118	91·934
10.	5·16313	4·74668	91·934
11.	5·08383	4·67374	91·933
12.	5·13372	4·71946	91·931
13.	5·16148	4·74490	91·929
14.	5·19919	4·77992	91·936
15.	5·37436	4·94088	91·934
		Average	91·933

Thus 100·000 parts of colourless argentic sulphate were found to yield 91·933 parts of argentic chloride, with a vanishingly small "probable error." If the weight of the darkened samples are used in the calculation the result becomes 91·934—a value which certainly represents the maximum. To have reduced the chief uncertainty to within such narrow limits was to have solved the problem as far as it need be solved at present. The interpretation of the result alone remains.

In comparing this result with that of Stas on argentic sulphate, it may be noted that Stas found in silver sulphate 69·203 per cent of silver. Because Richards and Wells found in argentic chloride $\frac{100{\cdot}000}{132{\cdot}867}\ 100 = 75{\cdot}2632$ per cent, it is clear that our results indicate 0·91933 × 75·2632 = 69·192 per cent of silver in silver sulphate, or 0·011 less than Stas's, one is forced to the conclusion that Stas's argentic sulphate was not completely reduced by hydrogen, and that his silver obtained in this way was no purer than the silver used in his other work. The only test of complete reduction used at the time was the solution of the residual metal in nitric acid; but this test could not reveal undecomposed sulphate and might not reveal traces of sulphide.

The Atomic Weight of Sulphur.

The interpretation of the new results is very similar to that already discussed in the paper on nitrogen and silver (CHEMICAL NEWS, xcvi., 180). In this case, as in that, there are two uncertain ratios; and one of these ratios, namely, that of silver to oxygen, occurs in each. In the present case, the other uncertain ratio is that of sulphur to oxygen, while in the former case the other uncertain ratio was that of nitrogen to oxygen.

In order to obtain a complete solution of the numerical relations in either of these cases, it is therefore obviously necessary to obtain another series of results, bringing in such a ratio as that of silver to sulphur, or oxygen to sulphur, or chlorine to oxygen. Such an additional ratio is not known at present with modern accuracy. Because of the fact that silver and oxygen are concerned in each of

the cases, a single new result, properly chosen, will solve both problems at once; but of course many new results with different compounds, confirming one another, are greatly to be desired. As has been said in the previous paper, some of these are already in the process of determination at Harvard College, and it is intended to pursue the matter further at the University of Berlin as well.

For the present it is necessary to state the interpretation of the results in a conditional manner, assuming various possible ratios between oxygen and silver, and stating the corresponding values for sulphur. In the future, when the assumed relationship is replaced by knowledge of the facts, intelligent choice can be made between the alternatives.

If oxygen is taken as 16·000, the following table gives the atomic weights of sulphur corresponding to the several atomic weights of silver.

Atomic Weight of Sulphur.

If Ag = 107·930 and Cl = 35·473, S = *32·113*
If Ag = 107·890 and Cl = 35·460, S = *32·078*
If Ag = 107·880 and Cl = 35·457, S = *32·069*

The lowest value in this case, as well as in the case of nitrogen, is the one supported by the recent work on the densities of gases.

In conclusion, it is a pleasure to acknowledge the generous assistance of the Carnegie Institution of Washington, without which the present work could not have been performed.

Summary.

The most important results of the research may be briefly summed up as follows:—

1. A method for the preparation of pure argentic sulphate was devised.
2. The specific gravity of argentic sulphate (previously fused) was found to be 5·45.
3. Indication was obtained that Stas was unable wholly to reduce silver sulphate in hydrogen.
4. Argentic sulphate was found to be occluded by silver chloride from solutions containing an excess of sulphuric acid.
5. It was proved that argentic sulphate can be completely converted into silver chloride by heating in a current of hydrochloric acid gas.
6. 100·000 parts of argentic sulphate were thus found to yield 91·933 parts of argentic chloride.
7. The atomic weight of sulphur as calculated from this ratio, if oxygen is taken as 16·000, with several assumed values for silver is—

Ag = 107·93	S = *32·113*
Ag = 107·89	S = *32·078*
Ag = 107·88	S = *32·069*

Attention is called also to the summaries of the three previous papers (CHEMICAL NEWS, vol. xcvi., pp. 148, 172, and 193).

Crystallised Iron Methylates.—K. A. Hofmann and Günther Bugge.—Methyl alcohol readily forms crystalline stable ferrites in the presence of acids, such as acetic or formic acid. Ethyl alcohol also possesses the same property to a less degree. Dimethoxyferric formate, $(CH_3O)_2FeO_2CH$, can be prepared by dissolving iron wire in strong formic acid and extracting the ferroformate obtained with methyl alcohol in an atmosphere of carbon dioxide. When the filtrate is exposed to the action of the air a yellow powder is precipitated. This powder consists of pointed double-refracting prisms of $(CH_3O)_2FeO_2CH$. Dimethoxyferric acetate, $(CH_3O)_2FeO_2C.CH_3$, is prepared similarly, using ferrous acetate instead of formate. When ethyl alcohol is used instead of methyl alcohol the solutions are, as before, readily oxidised in the air, but the products are very soluble. If the solutions are evaporated *in vacuo* a red powder remains behind, which contains only one ethoxy group, *i.e.*, the formula is $C_2H_5O.Fe(O_2C.CH_3)_2$.—*Berichte*, xl., No. 13.

USE OF FELSPATHIC ROCKS AS FERTILISER *

By ALLERTON S. CUSHMAN,
Assistant Director, Office of Public Roads, and Collaborator, Bureau of Plant Industry.

(Continued from p. 207).

The Availability of Potash in Ground Rock.

THE attention of the writer was first turned to the availability of potash in ground rock by a study of the decomposition which takes place when various rocks are used to form the surface of macadam roads. The binding power of rock dust depends upon the decomposition of the particles under the action of water and other substances. It has always been believed heretofore that only the potash that could be leached or dissolved out of a finely-ground material with water was available for plant growth. As a matter of fact, even the most finely-ground felspar which it is possible to obtain yields extremely minute quantities of potash to actual solution in water. Felspar which contained about 10 per cent of potash and was ground to a very fine powder yielded only 0·025 per cent to solution in water, and only 0·036 per cent to the action of a dilute acid. A large number of similar observations has led to the confident belief, almost universally held for many years, that although rocks which were disintegrated by natural processes served as the original source of potash, the action was so slow that it would be useless to grind rocks and attempt to use them as fertilisers. In the writer's investigations, however, evidence has been obtained which seems to show that decomposition of fine-ground felspar goes much farther than was indicated by the simple solution tests with water and dilute acids. By the use of laboratory methods it has been shown that almost complete decomposition can be made to take place in comparatively short periods of time under the action of water alone. In order to accomplish this result it has been necessary to use a method by which the potash is continually removed as fast as it is set free from its combinations in the rock. Now, as the roots of plants are continually performing this function, it is possible that in nature the decomposition of the felspathic particles in the soil must be continually going on as long as the product is being used, and slowing down to the stopping point when no removal is effected by plant growth. For further information on the scientific discussion of the decomposition of the felspars the original papers should be consulted (*Bull.* 92, Bureau of Chemistry, U.S. Dept. of Agriculture; *Cir.* 38 and *Bull.* 28, Office of Public Roads).

The fact, frequently cited and familiar to almost every person, that rocky hillsides with little or no soil can support growths of timber, would appear to demonstrate that rock potash is available. When it is remembered that wood ashes contain anywhere from 5 to 12 per cent of potash, it will be seen that a large tree represents, as it stands, a considerable quantity of this substance. However, trees take a long time to grow, and this present inquiry is mainly confined to availability in a single year from finely ground material.

In order to put the availability of the potash in very finely ground felspathic rocks to actual test the writer undertook some preliminary experiments in the greenhouse. Tobacco was selected for the experiments because, besides being extremely dependent upon an abundant potash supply, this plant is particularly well adapted to observation and control. Artificial soils were made up of clear, close-grained white sand and finely ground felspar, running about 8 per cent potash, such as is ordinarily prepared for use in the potteries, and which will pass through a standard sieve of about 200 meshes to the linear inch, having apertures approximately 0·0024 inch square. Tobacco seedlings were set out in this mixture and carefully fed from day to day with dilute solutions of ammonium nitrate and ammonium phosphate in order to supply the necessary amount of nitrogen and phosphoric acid. In addition to

* From *Bulletin* No. 104, U.S. Department of Agriculture, Bureau of Plant Industry.

this, a small amount of salts, containing lime, magnesia, and iron, was also added to the food solutions. Every care was taken, however, to see that no potash, except that which might be supplied by the felspar, obtained access to the plants.

For the sake of comparison, plants were also grown at the same time in a rich composted loam soil, which contained an abundance of all plant foods, including potash. Although the artificial sand-felspar soil was hard and apparently unsuited to the growth of plants, the tobacco nevertheless throve well in it, and showed at no time the slightest indication of potash starvation. When the experiments were finally abandoned, the tobacco plants growing in the sand felspar had attained a height of about 3 feet, and showed every indication of being as perfectly nourished as those growing in the rich soil.

In addition to the above experiments, seedlings were also set out in a poor, unfertilised soil, with and without the addition and admixture of a certain proportion of the ground felspar. Here also the availability of the felspar potash was clearly indicated.

These experiments, which were made in the summer of 1905, were not considered conclusive, but were sufficiently encouraging to justify further and more systematic investigation. Before proceeding it was of course necessary to look up the literature of the subject, in order to see to what extent ground felspar had been experimented with by other investigators. A Bulletin of the United States Department of Agriculture, which appeared a short time after the conclusion of the preliminary experiments described above, contains a partial reference list of previous publications along this line (*Bull.* 30, Bureau of Soils, U.S. Dept. Agriculture, p. 26).

On account of the great interest which has been aroused in this important subject and in order to present all the facts in the most accurate manner, the work of previous experimenters will be given in as much detail as space will permit. It is the intention to bring together all the information and evidence that the literature of the subject affords, whether it appears to be favourable to the use of ground felspar, or the reverse.

In 1849 Salm-Horstmar published in a German scientific journal (*Journ. Prakt. Chem.*, 1849, xlvi., 193) a method of preparing an artificial soil which, while being open, porous, and of a soft texture, should be absolutely free from all plant foods except those which were purposely added to it. The purest crystallised sugar was burned to a light form of charcoal and found to be absolutely free from any impurity capable of furnishing nourishment to plants. All sorts of different substances were then added to this material in other pots, and plants grown in them. In this way the experiments were kept under accurate observation and much information was obtained of the actual foods, and their forms, which are necessary to carry on the nourishment of plants. A short time after this investigation, in 1850, a chemist named Magnus repeated these experiments, and also made others (*Journ. Prakt. Chem.*, 1850, l., 65). In addition to the pots filled with sugar-charcoal, some of the pots were filled with coarsely pulverised felspar. It was found that the plants growing in the felspar made a good growth, even if no other food containing potash was added. The finer the felspar was ground the better was the development of the plants. Magnus summed up the results of his investigations as follows:—

1. In the absence of all mineral plant foods, barley attained a height of about 5 inches only before dying.
2. The addition of very small amounts of mineral plant foods enabled the plants to reach complete development.
3. If too much plant food was present, the plants were stunted or refused to grow at all.
4. In pure felspar barley made complete development and matured grain.
5. The development of growth varied with the coarseness or fineness of the felspar.

In 1861 Reichardt, a distinguished agricultural chemist, advanced the opinion that granite, porphyry, and other rocks rich in orthoclase felspar quickly give up their potash to plants when the particles are very fine ("Ackerbau Chemie," 1861).

About 1884 Hensel, a German writer and chemist, advocated the use of ground rock or so-called "stone meal," not only in order to supply the requisite potash, but also the phosphates and other mineral plant foods, such as lime, magnesia, iron, and manganese (A. J. Tafel, "Bread from Stones," 1894). This author published a philosophical work entitled "Das Leben," which treated in part of the use of rock fertilisers. Hensel thought that the use of excreta, offal, and other decaying and waste material as manure was harmful, if not to plants, at least to animals and men who subsisted upon them. Like many enthusiasts, Hensel appears to have been completely carried away by his ideas, which were not always justified by known facts. Hensel obtained, nevertheless, a considerable following and factories were established to prepare stone meal (Pomol, *Monatshefte*, No. 1, 1892; also *Wegweiser zur Gesundheit*, September 15, 1891). The subject evoked much discussion in Germany for many years. Whether rightly or wrongly, Hensel's ideas provoked the antagonism of nearly all the leading exponents of agricultural science in Germany. A great many experiments were undertaken, and in many cases the stone meal as prepared by the factories were shown to be very low in plant foods and nearly worthless as a fertiliser.

Among the prominent agricultural chemists who waged war on Hensel's stone meal were Wagner (*Zeit. Landw. Vereine Hessen*, 1894, lxiv., 14), Böttcher (*Centbl. Ag. Chem.*, 1895, xxiv., 363), Steglich (*Ibid.*, 1895, xxiv., 423), Hentschel (*Ibid.*, 1896, xxv., 136), Pfeiffer and Hansen (*Ibid.*, 1896, xxv., 802), and Morgen (*Ibid.*, 1898, xxvii., 743).

In some respects Hensel's arguments were not without weight, and he was keenly aware of the necessity for very fine grinding before the mineral constituents of rocks could be considered as practically available. The following quotation from a translation of Hensel's work stands for itself (A. J. Tafel, "Bread from Stones," 1894, p. 53).

"The practical point to settle is how far fertilising with stone meal pays, what yields it will afford; thus, whether it will be profitable for the farmer to use it. . . . It must here be premised that the fineness of the stamping or grinding and the most complete intermixture of the constituent parts are of the greatest importance for securing the greatest benefit of stone-meal fertilising. A manufactured article of this kind has recently been submitted to me which showed in a sieve of modern fineness three-fourths of the weight in coarse residuum. But as the solubility of the stone meal, and thus its efficiency, increases in proportion to its fineness, the greatest possible circumspection is required in grinding it. The finer the stone dust the more energetically can the dissolving moisture of the soil and the oxygen and nitrogen of the air act upon it. A grain of stone dust of moderate fineness may be reduced in a mortar of agate perhaps into twenty little particles, and then every little particle may be rendered accessible to the water and the air, and can, therefore, be used as plant food. Thence it follows that one single load of the very finest stone meal will do as much as twenty loads of a coarser product, so that by reducing to the finest dust, the cost for freight and carriage and the use of horse and cart would amount to only one-twentieth. Therefore we can afford to pay unhesitatingly a higher price for the finest stone meal that has been passed through a sieve than for an article that may be not so much a fine powder but rather a kind of coarse sand."

Inasmuch as this bulletin is interested mainly with the inquiry concerning the use of fine-ground felspar or felspathic rocks known to be rich in potash, no greater space need be given the German stone meal discussion.

(To be continued).

NOTICES OF BOOKS.

A History of Chemistry. By Dr. HUGO BAUER. Translated by R. V. STANFORD, B.Sc. (Lond.). London: Edward Arnold. 1907.

A SHORT history of chemistry containing in small compass, and at a moderate price, a complete account of the growth of the science from the earliest times to the present day will find a ready acceptance among those students who have not time for the study of the larger treatises on the subject, and Dr. Bauer's book will be found in many respects a useful addition to the chemists' library. It is well written, in simple and interesting language, and all the more important branches of the subject are at any rate touched upon. The chief defect is a want of balance with regard to the amount of space devoted to different periods and aspects of the science. Although the early years of its development are full of interest, the importance of the achievements of investigators before the time of Lavoisier would not, generally speaking, warrant the devotion of much space to their work and theories, when space is precious, while biographies of doubtful authenticity of early chemists, though they may add to the vividness of the narration, are not really worth the study of the young student. If the Periodic System cannot be accorded more than one page, twice this amount is too much to give to the biography of Paracelsus. Moreover, no accounts are given of the lives of many eminent modern workers, whose names are known all over the world, and, on the whole, too little attention is paid to the developments of recent years.

Précis d'Analyse Chimique Biologique Générale. ("Summary of General Biochemical Analysis"). By E. BARRAL. Paris: J. B. Baillière et Fils. 1908.

THIS work is a practical manual for physiologists, doctors, and chemists, describing methods of determining in the laboratory the substances contained in the organic tissues and liquids. Beginning with the albumenoids and going on to various nitrogenous derivatives, carbohydrates, fatty acids, &c., the general properties of each important substance, its characteristic reactions and methods of detection and determination are given. In every case the author has selected those methods which appear to him to combine simplicity with accuracy, and his experience of biochemical analysis enables him to give his readers a useful survey of the outlines of the subject upon which a detailed study of one or more of its branches could be based. Medical students in particular will find that the use of the book will enable them to economise in the time they give to the study of chemistry, because while they will avoid doing any general analysis which has no special bearing upon their medical work, nevertheless by the thorough investigation of animal products and tissues they will get an acquaintance with the manipulation and processes of analytical chemistry.

The Port of London and the Thames Barrage. By T. W. BARBER, M.Inst.C.E., and by C. J. DIBDIN, F.I.C., F.C.S., F.R.M.S., &c., E. T. HENNELL, M.Inst.C.E., CLAYTON BEADLE, F.R.Met.Socy., F.C.S., D. URQUHART. London: Swan Sonnenschein and Co., Ltd. 1907.

THIS book contains a series of expert studies and reports upon the conditions prevailing in the tidal river and estuary of the Thames. These studies include full accounts of the investigations of the engineer to the Thames Barrage Committee on the engineering aspects of the proposals which have been put forward with regard to the Port of London; moreover, papers on the infiltration from the Thames, the sanitary conditions of the river, &c., have been contributed by various experts, and the trade of the port is discussed. The writers establish clearly the practicability of the proposal of the construction of a barrage across the river in the neighbourhood of Gravesend, and although some of the economic aspects of the case for the present have had to be put on one side, the book at any rate provides opportunity for the public to acquire some knowledge of the probable effects of the proposed scheme.

CORRESPONDENCE.

THE FRUIT OF THE *CELESTRUS SCANDENS* AND *SOLANUM DULCARUM*.

To the Editor of the Chemical News.

SIR,—With reference to Messrs. Wells and Reeder's article on the above subject (CHEMICAL NEWS, vol. xcvi., p. 199), I think it is well to note that, in England, *Solanum dulcamara* is known as the "woody nightshade." and *Atropa belladonna* is the "deadly nightshade." There is no doubt Messrs. Wells and Reeder mean what we know as "woody nightshade," as they mention clusters of cherry-coloured berries.—I am, &c.,

ALBERT R. THORNWELL.

Highfield Road, Blackheath, Birmingham,
October 26, 1907.

To the Editor of the Chemical News.

SIR,—In Messrs. Wells and Reeder's article, *Solanum dulcamara*, whilst properly described in the text, is confounded with the "deadly nightshade." *Solanum dulcamara* is the woody or bitter nightshade, and is by no means so poisonous as the true deadly nightshade, whose berries are large, round, dark purple, and solitary, instead of "growing in clusters," "cherry-coloured," and "elliptical."—I am., &c.,

J. W. GATEHOUSE, F.I.C.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

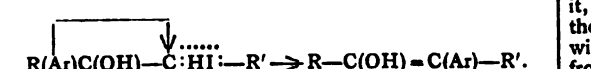
Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlv., No. 14, September 30, 1907.

This number contains no chemical matter.

No. 15, October 7, 1907.

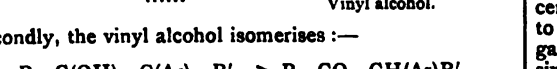
Migrations of Phenyl Group in Aromatic Iodohydrines by Elimination of Hydriodic Acid.—M. Tiffeneau.—The ethers of the aromatic iodohydrines (alkyliodohydrines, R(Ar)C(OAlk)—CHI—R') when treated with silver nitrate eliminate hydriodic acid and set free nitric acid, which hydrolyses the products of the transposition and converts them into aldehydes or ketones. Mercuric oxide, on the other hand, eliminates hydriodic acid, but leaves the medium neutral, and hence the products of the transposition are unaltered. Thus the author has proved that the transposition of these iodohydrines is effected in two stages. Firstly, the elimination of the

hydriodic acid causes the migration of the aromatic group, with the creation of a double bond :—



Vinyl alcohol.

Secondly, the vinyl alcohol isomerises :—



Berichte der Deutschen Chemischen Gesellschaft.
Vol. xl., No. 13, 1907.

Cobaltic Dioximes.—L. Tschugaeff.—When dimethyl glyoxime acts on bromine pentammino bromide the reaction which occurs may be represented by the equation

$$[Co_5NH_3Br]Br_2+2DH_2 = \\ =[CoNH_3BrD_2H_2]+2NH_4Br+2NH_3.$$

The bromine compound formed is a typical non-electrolyte. On re-crystallisation from hot water containing some acetic acid it forms large reddish brown coloured glittering needles. Methyl ethyl glyoxime gives with xantho or isoxantho salts, $[Co_5NH_3NO_2]X_2$, a crystalline compound, $[CoNH_3(NO_2)D_2H_2]$, which also behaves like a typical non-electrolyte. From roseopentammino-iodide, $[Co_5NH_3H_2O]I_3$, an iodine compound of dimethyl glyoxime, $[CoNH_3ID_2H_2]$, has been prepared; it is not so stable as the corresponding chlorine and bromine compounds, but it is readily converted into the iodide of the diammino series, $[Co_2NH_3D_2H_2]I$. The halogen compounds of the tetrammino series, $[Co_4NH_3Cl_2]Cl$ and $[Co_4NH_3Br_2]Br$, the praseo-salts; both react similarly with dimethyl glyoxime, but the isomeric croceo- and flavo-salts seem to behave differently. When a cobaltous salt reacts with dimethyl glyoxime in alcoholic solution in presence of pyridine an autoxidation process takes place, as represented by the equation—

$$2CoCl_2+4DH_2+4Py+O = \\ =2[CoPyClD_2H_2]+2PyHCl+H_2O.$$

This reaction also occurs in presence of *a*-picoline and other bases. In all the cases investigated brown or red-brown crystalline substances were obtained. They were usually hardly soluble in ordinary solvents (including water), and possess the properties of typical non-electrolytes.

Reductions with Amorphous Phosphorus.—Th. Weyl.—Under ordinary pressure phosphorus and hydrochloric acid have very little action on nitrobenzene at 100°, or even at 140°. In closed tubes, however, large quantities of bases are formed. These bases include aniline and also a good yield of solid *p*-chlor-aniline, rising to 75 per cent of the amount of nitrobenzene undergoing the reaction. Thus chlorine enters into the nucleus. To explain this striking reaction the author treated aniline with phosphorus and hydrochloric acid of specific gravity 1·19 first in open vessels at 100°, then in bombs at 140°, 170° and 190° to 220°, the action being allowed to last for ten hours; *p*-chlor-aniline was never obtained. Then the same experiments were performed with *p*-chlornitrobenzene, but again a negative result was obtained. However, *p*-chloraniline is formed by the action of hydrochloric acid on phenyl hydroxylamine and on nitrosobenzene. As both substances are very probably formed as intermediate products in the reaction between phosphorus, hydrochloric acid, and nitrobenzene, it is most likely that the formation of *p*-chlor-aniline is to be ascribed to these intermediate products.

Quantitative Expulsion of Phosphoric Acid from its Salts in a Current of Chlorine Saturated with Carbon Tetrachloride.—P. Jannasch and W. Jilke.—The apparatus for generating chlorine consists of a round flask of 2 to 3 litres capacity, a tubulated flask connected with it, and filled with caustic soda to absorb the chlorine when the experiment is finished, and a washing cylinder filled with concentrated sulphuric acid. The chlorine is made from 200 grms. of potassium permanganate and concentrated commercial hydrochloric acid, which is allowed to drop on the dry salt. With this quantity of permanganate a regular current of chlorine can be obtained for six hours. During the first three hours the reaction proceeds in the cold, and for the last part of the time the flask has to be heated. The chlorine is passed into an Erlenmeyer flask, which is warmed on a water-bath, and into which the carbon tetrachloride is allowed to drop slowly. The current of gases is then passed over the phosphate in a platinum boat heated in a combustion furnace, and the products received in water containing dilute nitric acid. After the combustion is over the liquid is collected in a porcelain dish, heated gently to drive off carbon tetrachloride, and then evaporated to a syrup. This is diluted and filtered, and the phosphoric acid present determined with molybdate.

Action of Sulphuric Acid on Phenol.—Jul. Obermiller.—Kekulé showed that when concentrated sulphuric acid acts upon phenol, phenol ortho-sulphonic acid is at first formed, and is rapidly converted into the *p*-acid on warming. These acids the author finds can easily be separated by converting them into mono-barium salts (SO_3H-salts). On evaporating the aqueous solution of these salts and cooling the concentrated liquid, the salt of the ortho-acid crystallises out first, and from the mother-liquor the mono-magnesium salt of the para-acid crystallises when magnesium sulphate is added. The acids can also be separated by a method based upon the different solubilities of the mono-magnesium salts. If the raw mixture of sulpho-acids is first converted into mono-magnesium salt and evaporated at a low temperature most of the *p*-acid crystallises out. The mother-liquor then gives with magnesia an alkaline OH-magnesium salt of the ortho-acid. Similar OH-barium and aluminium salts can also be prepared. All three salts give a violet iron chloride reaction. The author has investigated the process of sulphonation in detail, and the most important result of his work is the proof that ortho-substitution is favoured by low temperatures and also by using as dilute acid as possible.

Compounds of Ethyl Carbylamine with Cobaltous Chloride, Ferrous Chloride, and Ferric Chloride.—K. A. Hofmann and Günther Bugge.—The authors' experiments show that cobalt and nickel, as well as platinum, in the form of chlorides are capable of yielding solid double cyanides. They have prepared the following compounds in the crystalline state :—(1) Cobaltous chloride-dis-ethylcarbylamine, $CoCl_2,2C_2H_5.NC$; (2) ferric chloride-dis-ethylcarbylamine, $FeCl_3,2C_2H_5.NC$; (3) ferric chloride-tris-phenylcarbylamine, $FeCl_3,3C_6H_5.NC$; (4) oxydiferric chloride-tetrakis-ethylcarbylamine, $OFe_2Cl_4,4C_2H_5.NC$; (5) oxydiferric chloride - pentakis - ethylcarbylamine, $OFe_2Cl_4,5C_2H_5.NC$.

Compounds of Salts of the Dichloro-chromium Base with Ammonium Salts.—R. F. Weinland and Theodor Schumann.—If ordinary green chromium chloride hydrate, $[CrCl_2(4H_2O)]Cl.2H_2O$, is dissolved in a 35 per cent solution of ammonium sulphate, a green salt, $CrCl_3.2SO_4(NH_4)_2.6H_2O$, separates after a short time. In it one chlorine atom is dissociated in aqueous solution and precipitated by silver nitrate in nitric acid solution. The SO_4 is precipitated by barium chloride. This salt corresponds to Werner's double salt of chromium chloride and cæsium chloride, $CrCl_3.2CsCl.4H_2O$. According to Werner, the two molecules of cæsium chloride take the place of two molecules of water of the hydrate which have escaped *in vacuo* over sulphuric acid. The ammonium sulphate double salt contains two molecules of ammonium sulphate, and should thus contain only four molecules of water in addition, whereas six are present; this might be

due to the sulphuric acid, for sulphates contain more water than can be explained by Werner's hydrate theory. However, a sulphate, $[CrCl_2.4H_2O]\frac{SO_4}{2}.(SO_4)_2(NH_4)_3H$, has been obtained by adding sulphuric acid to the solution of ammonium sulphate and chromic chloride. Moreover, an ammonium chloride chromic chloride obtained by the authors also contains six molecules of water.

New Plant Alkaloids.—Amé Pictet and G. Court.—The authors have studied the alkaloids which can be isolated from the five plants tobacco, black pepper, cultivated carrot, parsley, and cocoa, and find the presence of more or less completely hydrated pyrrol nuclei in all the bases obtained. This analogy in chemical composition seems to point to a common origin of these bases, and shows that they are the decomposition products of one and the same mother substance in which the pyrrol nucleus is present. Emil Fischer, Küster, and Nencki have shown that this nucleus is present in the molecule of albumen and chlorophyll, and since in the latter it is probably condensed with a reduced aromatic ring, forming an iso-indol complex, and since it is hardly probable that it would be readily split off from such a complex, it must be concluded that the pyrrol bases in these plants are formed from vegetable albumen. Moreover, probably these simple bases must be regarded as the proto-alkaloids, from which, by various transformations (methylation, condensation, &c.), complicated alkaloids are formed. Since the plants examined were chosen at random and belonged to five different families, possibly the formation of these bases is due to a general biochemical process which occurs in all plants.

Chemistry of Hydrosulphites.—A. Binz and Th. Marx. — Benzoyl chloride gives with potassium oxalate, sodium nitrite, and soda, *i.e.*, with easily decomposed bases, benzoic acid anhydride, $2C_6H_5.COCl + Na_2CO_3 = 2NaCl + CO_2 + (C_6H_5.CO)_2O$. The same reaction occurs in presence of pyridine. Sodium hydrosulphite also gives benzoic acid anhydride, but, if no pyridine is present, in addition benzoyl disulphide is obtained. When pyridine is present, a red crystalline base of formula $C_{11}H_{10}N_2S$ is also formed, as well as a yellow compound which can readily be converted into the red base. Hydrosulphite behaves partly by sulphoxalate and partly like sulphite. When sodium sulphite reacts with benzoyl chloride, benzoyl disulphide is not formed. Thus this is a sulphoxylate reaction. As sulphur always separates, it is probable that it also plays some part in the reaction. Sulphur itself has no action on benzoyl chloride at 230°, but sodium sulphide might be formed from the hydrosulphite, and then give rise to the following reaction:— $2C_6H_5.COCl + Na_2S + S = 2NaCl + (C_6H_5.CO)_2S_2$. Benzoic acid anhydride, the red and the yellow substances, are formed both from hydrosulphite and from sulphite. The red substance is very easily combustible; analysis shows that in it two pyridine residues and a sulphur atom are connected with one another. The rôle of the benzoyl chloride in the reaction has not been explained. The yellow base has the formula $C_{23}H_{16}N_4S_4O_6$, but it cannot be re-crystallised; it is either not taken up by ordinary solvents or else it is converted into the red base.

MEETINGS FOR THE WEEK.

MONDAY, 4th.—Royal Institution, 5. General Monthly Meeting.
—— Society of Chemical Industry, 8. "Determination of Indigotin in Indigo-yielding Plants," by C. Bergtheil and R. V. Briggs. "Analysis of Indigo and of the Dried Leaves of *Indigofera Arrecta* and *Indigofera Sumatrana*," by R. Gaunt, F. Thomas, and W. P. Bloxam.

WEDNESDAY, 6th.—Society of Public Analysts, 8. Discussion on the Sealing of Samples. Members and their friends will meet to dine at the Comedy Restaurant, Panton Street, Haymarket, at 6.15.

THURSDAY, 7th.—Chemical, 8.30. "Gaseous Nitrogen Trioxide," by H. B. and Miss M. Baker. "Atomic Weight of Tellurium," by H. B. Baker and A. H. Bennett. "Isomerism of the Double Sulphites of Sodium and Potassium," by M. H. Godby. "Studies in the Camphane Series—Part XXIV., Camphoryldithiocarbamic Acid and Camphorylthiocarbimide," by M. O. Forster and T. Jackson. "The Vhpour pressures of Triethylamine, of *sym*-Trimethylpyridine, and their Mixtures with Water" and "Liquid Triethylamine," by R. T. Lattey. "Action of Sulphuretted Hydrogen on Solutions of Sodium Hydrosulphite," by F. S. Sinnatt. "Alkyl Compounds of Gold—Diethylauric Bromide," by W. J. Pope and C. S. Gibson. "Constitution of Homoeriodictyol," by F. B. Power and F. Tutin. "Interaction of Methylene Chloride and the Sodium Derivative of Ethyl Malonate," by F. Tutin. "Preparation of Aliphatic Nitro-compounds by the Interaction of the Alkyl Iodides and Mercurous Nitrite," by P. C. Ray and P. Neogi. "Some Mercury Derivatives of Camphor," by J. E. Marsh and R. de J. F. Struthers. "Chemistry of the Terpenes—II., The Oxidation of Limonene with Chromyl Chloride," by G. G. Henderson. "Synthesis of Acridines and Phenonaphthacridines—Tetra- and Hexa-methylacridines, Dimethylphenonaphthacridines, Dixylylmethylenediamines," by A. Senier and A. Compton.

FRIDAY, 8th.—Physical, 8. Discussion on Mr. Campbell's paper on the "Use of Variable Mutual Inductances." "A Graphic Method for Stream-lines and Equipotential Surfaces," by L. F. Richardson. "Lateral Vibrations of Bars supported at Two Points with one End Overhanging," by J. Morrow.

ERRATUM.—P. 188, col. 1, line 34, *for* "$6L_3$" *read* "bL_3."

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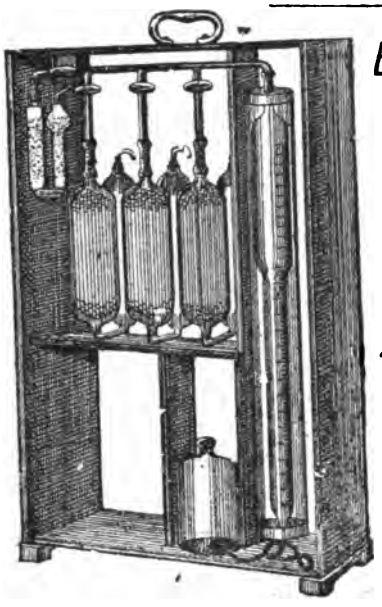

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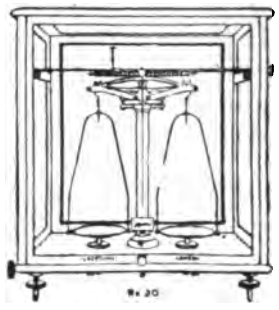

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THE CHEMICAL NEWS.

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A NEW METHOD SUGGESTED FOR DETERMINING VAPOUR-DENSITIES.

By PHILIP BLACKMAN.

THE apparatus consists of a vessel having a tight-fitting stopper at one end and at the opposite end a long capillary tube with a tap at its end. (The tap is such that when turned off its "blade" is in line with the capillary). By means of a split cork it can be inserted in a flask fitted with a condenser (Fig. 1). The volume of the vessel is

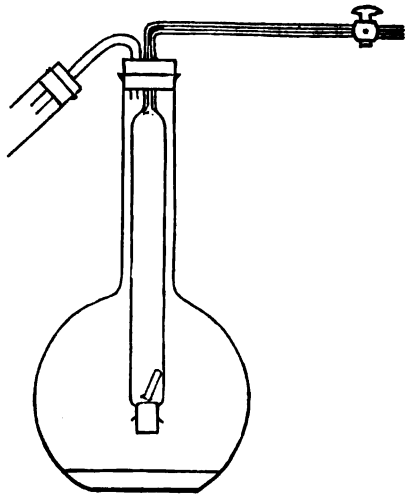


FIG. 1.

determined once for always, and also that of the capillary, the latter being graduated. A short thread of mercury is introduced to close the tap, and another near the body of the vessel; the air space between the two threads will serve as a pressure gauge. A weighed quantity of the substance to be experimented on is introduced in a small tube, the stopper fixed and tied firmly to the neck with wire, the whole fixed in the flask, and finally heated in the vapour of some liquid boiling at a temperature above the boiling-point of the substance (if water be employed as the heating liquid, the use of a condenser may be dispensed with). It will be observed that solid substances which can be vaporised can be dealt with by this method. The final readings are taken when the volume of the air in the gauge remains constant.

Let ρ = atmospheric pressure;
t_1 = initial temperature;
t_2 = temperature of vapour;
t_3 = mean temperature of the gauge;
t_4 = mean temperature of the space between the vessel and the first mercury thread;
L = initial volume of the air gauge;
l = final volume of the gauge;
H, h = respectively the initial and final volumes of the space between the vessel and the first mercury thread;
V = volume of the vessel;
w = weight of substance.

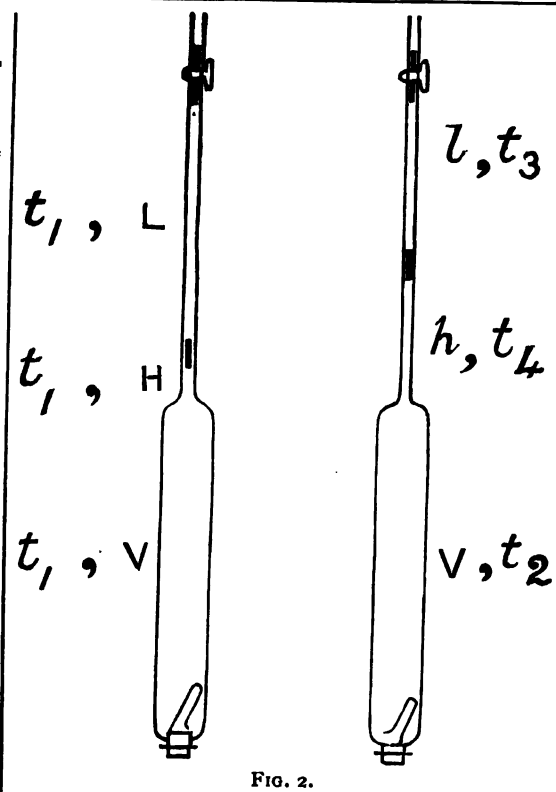


FIG. 2.

Pressure of air in gauge $= \rho L(273+t_3)/l(273+t_1)$; pressure of air in space $V = \rho(273+t_2)/(273+t_1)$; pressure of air in space $h = \rho H(273+t_4)/h(273+t_1)$; hence the pressure due to the vapour

$$= \frac{\rho}{273+t_1}\left[\frac{L}{l}(273+t_3) - (273+t_2) - \frac{H}{h}(273+t_4)\right] = \pi.$$

The volume of the vapour at 0° and 760 mm.

$$= \frac{\pi V 273}{760\,(273+t_2)} + \frac{\pi h 273}{760\,(273+t_4)} = v.$$

Therefore the density of the vapour at 0° and 760 mm.—

$$= \frac{w}{v}$$

$$= \frac{760\, w\, (273+t_1)}{273\rho\left(\frac{V}{273+t_2} + \frac{h}{273+t_4}\right)\left(\frac{L}{l}[273+t_3] - [273+t_2] - \frac{H}{h}[273+t_4]\right)}$$

From this a comparison with the vapour-density of hydrogen at 0° and 760 mm. may be made.

The calculation and manipulation will be much simplified if the apparatus be of the form shown in Fig. 3. (The apparatus shown in Fig. 4 has the advantages of greater sensitiveness of the air gauge due to its greater length and increased capacity of the volume V). The whole apparatus can thus be introduced into the vapour of the boiling liquid by suspending it with wire from the cork.

In this formula we have $t_2 = t_3 = t_4$, and the formula for the vapour density thus becomes—

$$\frac{760\, w\, l\, (273+t_1)}{273\,\rho\,(V+h)\left(L - l - \frac{H\,l}{h}\right)}.$$

In practice it should be found easy to so manipulate the

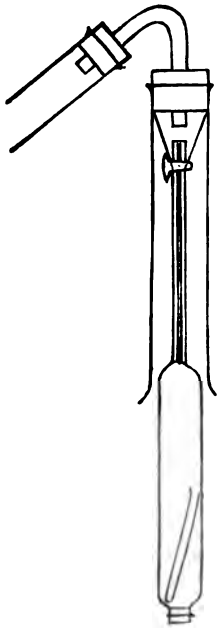


FIG. 3.

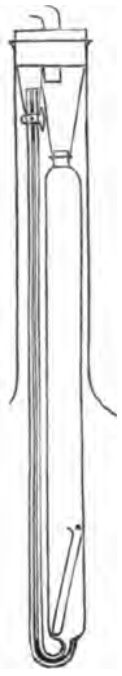


FIG. 4.

threads of mercury as to make H = o, and thus the formula last given becomes—

$$\frac{760\, w\, l\, (273 + t_1)}{273\, \rho\, (V + h)(L - l)},$$

or (as h is generally very small compared with V, and may thus be neglected for ordinary purposes)—

$$\frac{760\, w\, l\, (273 + t_1)}{273\, \rho\, V\, (L - l)}.$$

ON THE ELECTROLYSIS OF SALT SOLUTIONS IN LIQUEFIED SULPHUR DIOXIDE AT LOW TEMPERATURES.*

By BERTRAM D. STEELE, D.Sc.

THE investigation of which this is a preliminary notice is a natural continuation of the research started by Dr. M'Intosh and myself in 1903. The investigation has for its object the study of the electrolysis of salts dissolved in certain liquefied gases, and of the products formed during electrolysis. The first system that has been investigated is that of a solution of potassium iodide dissolved in sulphur dioxide, and a large number of experiments extending over several months have been carried out.

My attention having been called to a proposed investigation along similar lines by Giuseppe Magri, of which an abstract appears in the *Journal of the Chemical Society* (xcii., p. 237, April, 1907), I thought it best to publish the following brief summary of the conclusions that have been so far arrived at :—

1. When a nearly saturated solution of potassium iodide in sulphur dioxide is electrolysed between electrodes consisting of thin platinum wires, and with a potential difference of between 10 and 20 volts, a current of about 80 to 100 milliampères is obtained during the first instant. The current immediately begins to fall rapidly to a value considerably less than 1 milliampère. With a potential difference of about 40 volts apparent gas evolution occurs (possibly ebullition of sulphur dioxide), and on breaking the circuit a polarisation E.M.F. of over 1 volt is obtained.

2. With larger platinum electrodes the fall in current is much slower, but after several hours falls to a similar extremely low value. In this case a scarcely detectable polarisation voltage can be observed.

3. Similar results are obtained when mercury electrodes are used, but the fall in current is not so marked.

4. With platinum and mercury electrodes the current, which is extremely variable and inconstant, appears to depend on the previous history of the electrodes.

5. It has been found that a constant and consistent current can be obtained by using a silver, copper, or iron cathode of large area.

6. The following changes occur at the anode :—
   When a platinum anode is used iodine is liberated and dissolved in the surrounding solution.
   When a zinc anode is used no iodine is liberated, and the solution remains yellow in colour. It is probable that zinc iodide is formed and dissolved in the solution.
   When an iron anode is used no iodine is liberated, but the solution surrounding the anode becomes blackish green in colour.
   When a mercury anode is used mercurous iodide is formed and precipitated, forming a layer on the electrode which appears to cut off the current.

7. The following changes occur at the cathode :—
   When currents of 20 milliampères and over are used with a platinum cathode there is formed a dark coloured crystalline deposit, which on drying in an atmosphere of dry sulphur dioxide becomes white. Small quantities of sulphur are always found mixed with this deposit.
   The deposit on analysis was found to have a composition very closely corresponding with that required for potassium sulphite, in some cases being, however, much richer in sulphur dioxide.
   The platinum cathode, if very small currents are used, is still coated with the potassium sulphite compound, but contains little, if any, admixed sulphur, which is, however, in all cases found dissolved in the solution surrounding the cathode.
   The extraordinary manner in which the current falls after the first few moments is thus accounted for by the deposition of a thin film of insulating sulphur on the surface of the cathode.
   The deposition of sulphur is prevented by using either a silver or a copper cathode. Under these circumstances a black deposit is formed on the cathode. This deposit is probably silver sulphide or copper sulphide, as the case may be, and as both of these are conducting substances the current is not seriously diminished.
   No evidence has yet been obtained of the deposition of potassium as metal on the cathode.

8. By means of a specially constructed piece of apparatus the conductivity of the solution in the neighbourhood of the cathode was determined during the progress of the experiment, and in all cases an increase of resistance was observed.

In the same way as the liberation of hydrogen at the cathode during the electrolysis of a solution of potassium iodide in water is regarded as evidence of the occurrence of hydrogen cations in the aqueous solution, so the liberation of sulphur at the cathode in the foregoing experiments indicates the occurrence of sulphur cations in a solution of potassium iodide in sulphur dioxide, and similarly the formation of what is probably potassium sulphite in the latter system is analogous to the formation of potassium hydroxide in the former.

* A Paper read before the Faraday Society, October 29th, 1907.

The following is a possible representation of the changes which take place :—

$$S:: + 4\ominus = S$$
$$4K^{\cdot} + 2O'' + SO_2 = 2K_2SO_3,$$

the sulphur and the potassium sulphite being deposited together at the cathode.

This would explain not only the formation of these two substances but also the observed diminution in conductivity of the solution immediately surrounding the cathode.

9. After the necessary conditions for obtaining a steady current had been worked out, a special apparatus was designed and constructed for the measurement of ionic velocities of the ions in sulphur dioxide solution, and a few preliminary measurements have been made with this apparatus.

It is intended to extend these measurements and to thoroughly investigate this and other similar systems.

NOTE ON THE

SOLUBILITY OF BISULPHITE COMPOUNDS OF ALDEHYDES AND KETONES.

By JOHN B. COPPOCK, B.Sc. (Lond.), F.I.C., F.C.S.

It has been noticed that students working the bisulphite reactions for the lower aldehydes and ketones fail to get the usual precipitates, consisting of the bisulphite and the aldehyde, or ketone, if a solution of the bisulphite be made by saturating a sodium carbonate solution with sulphur dioxide gas. The solution used has been a saturated one of the bisulphite, made as above, and having a deep yellow, much like potassium chromate solution.

If, on the other hand, a saturated solution of the bisulphite, made by dissolving this salt in hot water and then cooling, be added to the compounds under consideration the usual precipitate is obtained.

This difference suggested the probability of the compounds being soluble in sulphur dioxide; to see if this is the explanation the following experiments were made:—

Acetaldehyde.—Saturated solution of bisulphite added, and precipitate obtained. The precipitate, with the solution, was subjected to a stream of sulphur dioxide gas, when it finally dissolved.

Acetone.—This was treated precisely as above, and sulphur dioxide on being passed again dissolved the precipitate.

The precipitates were also subjected to a golden yellow solution made as described in the first paragraph; this in each case dissolved the precipitate.

Very plainly it seems that in making a saturated solution of a bisulphite from washing soda the sulphur dioxide gas should not be passed until the liquid is strongly smelling of it. A very pale green tint seems to be the point where the sulphur dioxide should be cut off.

Chemical Laboratory, Kendal.

FURTHER ANALYSES OF CONDENSED MILK.

Report by F. J. LLOYD, F.C.S., Consulting Chemist to the British Dairy Farmers' Association.

When I received instructions to make analyses of another five samples of condensed milk, and this time not to confine myself to machine-skimmed milk, I endeavoured to obtain samples of full-cream milk from the same sources as I had obtained the machine-skimmed. It must be clearly remembered that I had not bought these former samples as or knowing them to be machine-skimmed, but had simply asked for the brands of which they sold the greatest amount, and it was only after purchasing the samples that I found in all cases they were machine-skimmed. Now upon attempting to obtain samples of full-cream milk I was met with two difficulties: First, that in many of these places nothing whatever was kept but condensed machine-skimmed milk; and, secondly, that after numerous efforts in various places I could only find three full-cream condensed milks on the market. Subsequently I obtained Sample A 89 (unsweetened), and also Sample A 88, which I had not previously examined, and which appears to be the cheapest machine-skimmed milk on the market. It is only fair to state that the makers of this brand print on the label surrounding the tin—"Unsuitable for the use of infants and invalids."

As regards the composition of the samples themselves, nothing need be said; they all represent milk reduced to about one-third its volume, so that to bring it back to the richness of ordinary milk as regards fat and other solids, one part of these milks could be mixed with only two parts of water. It will be seen that, even taking the first two samples, 45 ozs. of milk would cost 5½d., *i.e.*, for a little over a quart of milk, which is a much higher price than the same quantity of milk can be bought for in a fresh condition. There can, I think, be no doubt whatever that the people who use condensed milk dilute it to such an extent that it becomes practically a mixture of equal parts of milk and water. Indeed, on one of the tins the directions state that for puddings, coffee, tea, &c., the milk may be diluted with four or five times its volume of water.

	A 85.	A 86.	A 87.	A 88.	A 89.
Nature	Full cream	Unskimmed Swiss	Full cream	Machine skimmed	Full cream, unsweetened
Prepared in	England	Switzerland	Switzerland	Holland	Norway
Contents of tin	15 ozs.	15 ozs.	14½ ozs.	13 ozs.	12 ozs.
Price of tin	5½d.	5½d.	5½d.	2d.	4½d.
Analysis—Water.. ..	18·70	13·04	16·52	26·14	67·72
Fat	9·94	11·13	8·20	1·02	10·13
Casein . ..	10·95	8·37	9·90	8·43	10·86
Sugar, &c...	58·21	65·46	62·54	62·41	9·55
Ash	2·20	2·00	2·84	2·00	1·74
	100·00	100·00	100·00	100·00	100·00
Containing boric acid..	0·17	0·10	None	None	None

The Society might endeavour to discover how far the condensed milk used in or imported into England consists of full-cream or machine-skimmed milk. I think also that some steps should be taken to draw the attention of the medical profession to the composition of condensed milk, and to the danger which must arise from infants being fed upon it. Probably much of the ill-health among children, frequently attributed to the consumption of impure fresh milk, if investigated, would be found to be due to the use of condensed machine-skimmed milk. It is very doubtful whether the vast majority of the poor people who buy and use this condensed machine-skimmed milk have any knowledge of what they are using. They simply buy what is cheapest, and make it go as far as they possibly can, without any regard to the health of their infants.

Laboratory.
Muscovy House, Trinity Square, London, E.C.,
September, 1907.

THE

USE OF FELSPATHIC ROCKS AS FERTILISERS.*

By ALLERTON S. CUSHMAN,
Assistant Director, Office of Public Roads, and Collaborator, Bureau of Plant Industry.

(Continued from p. 219).

The Availability of Potash in Ground Rock (continued).

Some experiments were carried out in 1887 on the use of ground felspar as a fertiliser by Aitken, a Scotch agriculturist, and chemist to the Highland and Agricultural Society of Scotland. Aitken does not say that he was aware of the work of Magnus or the deductions of Hensel. The record of these experiments is given in the author's own words (*Trans. Highland and Ag. Soc. Scotland*, 1887, Series 4, xix., 253) :—

"We are familiar with the fact that felspar, under the slow but constant action of those forces included under the name of weathering, becomes disintegrated and decomposed, and that the potash it contains is dissolved away from it by rain, so that streams emanating from districts where felspathic rocks abound are found to contain potash salts, and the level straths laid down by the prolonged action of these streams yield fertile soils that are rich in potash. These soils are the product of natural agencies that have been going on for centuries, and the store of soluble potash salts they contain has been increased to an untold extent by the slow solvent action of the roots of plants that have grown on them, so that the conversion of felspathic rock into soil so rich in potash as to afford an abundant supply of that constituent for the raising of agricultural crops is the product of the work of centuries. At first sight, it might seem a foolish thing to expect that by merely grinding felspathic rock, and strewing the powder upon soils deficient in potash, the long natural process referred to should be so accelerated as to cause the felspar to act as a source of potash for the immediate use of the growing of crops whose vigorous growth demands a relatively large amount of that substance. Nevertheless, the striking results of an experiment made at the Society's experiment station at Pumpherston showed that such an expectation was not altogether unreasonable. Ground phosphates had been used as a phosphatic manure with varying success for some years, and as it seemed that the varying nature of the results obtained might be due to the varying degrees of fineness to which phosphates were ground, I made a small preliminary experiment, in which the same phosphate was applied in different degrees of fineness, and I found that the more finely ground the phosphate the more effective was it as a manure. A similar experiment on a larger scale is described in the *Transactions*, p. 245, where it is seen that the efficiency of ground phosphates is in direct proportion to their fineness. It therefore seemed reasonable to suppose that felspar, although it is a very insoluble substance, might, if it were ground to an exceedingly fine powder in certain circumstances, be found to yield to the action of the solvents in the soil and in the roots of plants so rapidly as to be available as a source of potash to some crops, even during the short period of a single season.

"Accordingly I obtained, through Mr. Bödker, the Swedish and Norwegian consul here, at whose instigation the experiment was undertaken, a supply of very pure felspathic rock, rich in potash, of which enormous quantities are to be had in Norway. It was ground as finely as possible by Messrs. J. & J. Cunningham, of Leith, and thereafter sifted through a sieve of 120 wires to the linear inch, and was found to contain about 12 per cent of potash. The whole quantity of sifted felspar was very small, less than a half hundredweight, and as it was received late in the season, the experiment was made simply to afford information which might indicate whether it was desirable to try the experiment on a larger scale the following season. There were two small experiments made—one by Mr. R. Shirra Gibb, at Boon, on a crop of peas, and one at Pumpherston on turnips. The experiments were on plots of one-fortieth acre, and the following were the manures employed and the results obtained :—

	Kind and quantity of fertilisers.	Peas. Dried in bulk. Lbs.	Peas. Grain. Lbs.	Turnips. Bulbs. Lbs.
1	Sulphate of potash, 3 lbs. Sulphate of lime, 3 lbs. .. Superphosphate, 6 lbs. ..	114	3·8	482
2	Ground felspar, 12 lbs. .. Sulphate of lime, 3 lbs. .. Superphosphate, 6 lbs. ..	102	3·5	496
3	Sulphate of lime, 3 lbs. .. Superphosphate, 6 lbs. ..	96	—	476

"Although the whole experiment is on a small scale, and the crops are below the average, there is nevertheless a clear indication that the felspar has acted as a potash manure. In both cases where no potash was applied the crop is the smallest. At Boon the plot with no potash was unable to mature its seed, so that it could not be thrashed, while on the other two plots the amount of seed was not very different, and quite in proportion to the total crop, viz., about one-fortieth. The smallness of the crop does not detract from the value of the experiment as a means of indicating whether or not felspar acts as a potash manure. Had the crop been sown at the proper time it would have been much larger. In the case of the turnip crop the ground felspar has done better than the sulphate of potash. That may be accidental, but it may be that the insoluble form in which potash is contained in felspar is more favourable for turnip growing than the soluble sulphate. Soluble potash manures, when applied to the turnip crop, sometimes diminish rather than increase the crop, and this is especially the case where the crop is dunged in the drills; but no dung has been put on the Pumpherston station these twelve years, and the results obtained all over the field show that potash is now required for turnip growing on that land.

"Upon the whole, the result of this experiment may be taken as showing that potash felspar when ground to an exceedingly fine powder is capable of acting as a potash manure even in a single season."

In 1889 the Maine State experiment station, under Balentine, independently of any previous experimenters, investigated the use of ground felspar as a source of potash on oats ("Annual Report Maine State Col. Exp. Station," 1889, p. 143). The results are given verbatim from the records of the station :—

"In connection with the experiments with finely ground phosphatic rock as a source of phosphoric acid for plants, pot experiments have been undertaken to determine to what extent plants can avail themselves of the potash of potash felspars. The pots used for the experiments were like those used in the phosphate experiments. They were also filled in the same manner, having first a layer of gravel at the bottom and above this 65 pounds of quartz sand, with the last 35 pounds of which were mixed the experimental fertilisers.

"Three pots, 1, 5, and 9, were supplied each with 10 grms. of felspar carrying 11·61 per cent of potash, 10 grms. of nitrate of soda, and 10 grms. of acid South Carolina rock. Three other pots, 13, 17, and 20, were fertilised with 20 grms. of felspar and the same amount of nitrate of soda and acid phosphate as was supplied to 1, 5, and 9. In these pots were planted oats. When the oats were 2 or 3 inches high they were thinned out to 18 plants per pot. The pots were watered in the same manner as were those in which the experiment with phosphates was conducted.

* From *Bulletin* No. 104, U.S. Department of Agriculture, Bureau of Plant Industry.

TABLE A.—*Weight of Crop of Oats from Seven Plats of 100 Plants each, Grown with various Fertilisers.*

No.	Kind of Fertiliser.	Grain. Grms.	Straw. Grms.	Chaff. Grms.	Total. Grms.	Equivalent yield of grain per hectare. Kilogrms.
1.	Unfertilised	5·3	11·0	1·0	17·3	216
2.	Phosphate and potassium sulphate	157·3	220·5	16·3	394·1	6400
3.	Phosphate and 300 felspar potash	133·8	178·7	15·5	328·0	5450
4.	Phosphate and Chili saltpetre	175·5	242·8	21·2	439·5	7150
5.	Phosphate, Chili saltpetre, and potassium sulphate	232·5	346·2	24·8	603·5	9470
6.	Phosphate, Chili saltpetre, and 200 felspar potash	171·5	245·2	21·3	438·0	7000
7.	Phosphate, Chili saltpetre, and 300 felspar potash	177·7	262·5	23·5	463·7	7240

"In the table below are shown the results of substituting muriate of potash for felspar as a source of potash :—

Kind and quantity of fertilisers.	No. of pot.	Yield of grain. Grms.	Yield of straw. Grms.
10 grms. felspar	1	18·37	47
10 grms. nitrate of soda	5	14·37	43
10 grms. acid South Carolina rock	9	19·43	47
20 grms. felspar	13	17·28	47
10 grms. nitrate of soda	17	16·78	47
10 grms. acid South Carolina rock	21	16·83	52
3 grms. muriate of potash	16	22·88	67
10 grms. nitrate of soda	20	18·85	72
10 grms. acid South Carolina rock	24	24·37	65

"The pots receiving 10 grms. of felspar produced, on the average, about 79 per cent of the average of the grain produced by those pots receiving 3 grms. of muriate of potash having 50 per cent of actual potash. The amount of grain was not increased by increasing the felspar to 20 grms., though there was a slight gain in straw.

"The conclusion to be drawn from the expetiment is that the oats were able to draw from the felspar potash enough for a large crop of grain. If this conclusion is verified by future work, some of our felspars may prove a cheap source of potash to the farmers of the State."

Examination of the figures given in the above table shows that the potash from the felspar undoubtedly became available, but was not as efficient as that from the more soluble muriate.

In 1889, the same year that the results of these experiments were made public, Nilson in Sweden published an investigation in which fine-ground felspar prepared for the potteries was tested in comparison with potassium sulphate ("Landtbr. Akad. Handlingar och Tidskr.," 1889; see also *Centbl. Ag. Chem.*, 1889, xviii., 608). Oats were used, and the experiments were carried out on the Swedish moor soils, which, in a dry condition, already contained 0·5 per cent of potash, although only 0·03 per cent of this was soluble in dilute acid. There were 300 kilogrms. (660 pounds) of slag phosphate, 50 kilogrms. (110 pounds) of nitrogen in the form of Chili saltpetre, and 80 kilogrms. (176 pounds) of potash as sulphate or 200 to 300 kilogrms. 440 to 660 pounds) as ground felspar added to the hectare (2·47 acres). The results of weighings of crop yield, made on the basis of 100 plants from each trial, are given in Table A.

Nilson's results are most unfavourable to ground felspar, as an inspection of the figures shows, but as a very good yield was obtained by the use of Chili saltpetre and phosphate without any additional potash, the experiments are not very conclusive. Chili saltpetre is a crude nitrate of soda which sometimes contains potash salts. It is possible that in all these experiments there was a tendency to overfeeding rather than to underfeeding.

In 1890 Sestini published the results of a very interesting investigation of the decomposing action of plant roots on felspar (*Landw. Vers. Stat.*, 1900, liv., 147). A coarse felspathic granite sand from the island of Elba was first carefully washed to remove all adherent earth or plant food, and then mixed with certain amounts of carbonate, phosphate, and sulphate of lime. The nitrogen was supplied in the form of ammonium nitrate. Various plants and grasses were grown in this mixture under very careful test conditions. The crops matured well, and at the end of about a year it was shown that a very considerable decomposition of the felspar had taken place. Sestini concluded that the decomposition of the felspar went on much more rapidly under the influence of plant growth than had previously been supposed.

In 1901 Headden, working at the Colorado Experiment Station, also independently, carried on some interesting experiments on the availability of potash contained in ground felspar (Colorado Experiment Station, *Bull.* 65, p. 30). To quote this author's own words :—

"We endeavoured to determine whether the felspar could furnish potash to plants. For this purpose fresh mineral was used, pulverised as already described in imitation of the soil, *i.e.*, the particles varied from 1 mm. in diameter to an impalpable powder. This was mixed with pure quartz sand. Bone-ash was used to supply lime and phosphoric acid. The sample used contained no potash. Nitrate of lime furnished the nitrogen. Chlorine was furnished by a minute quantity of calcic chloride. Distilled water was used throughout the experiment.

"The plants grew healthily in this mixture until the floors of the building were oiled, and the room in which the plants were growing was shut up and became too warm; these two things together gave them a decided setback, and later a thrips, *Thrips striata* according to Prof. Gillette, attacked the plants, and did them much damage. Some of the plants, however, seeded. They were harvested, though in bad condition, and very uneven in the degree of their development. The root system was well developed, the sand being filled with the roots. The weight of the tops as harvested was 198·5 grms.; that of the roots as washed out was 40 grms. The tops and roots were incinerated together, and yielded 5·795 per cent of soluble and 9·803 per cent of insoluble ash, a total of 15·598 per cent.

"Examination of the felspars used showed the presence of 11·993 per cent of potash and 2·988 per cent of soda. Phosphoric and sulphuric acids were present in very small quantities; the former equalled 0·041 per cent and the latter 0·003 per cent of the felspar.

"The nitrogen in the oat hay, roots included, was 3·2543 per cent.

"The ash gave the following analysis :—

Carbon	0·17 per cent
Sand	8·13
Silicic acid	15·73
Sulphuric acid	4·41
Phosphoric acid	3·98
Carbonic acid	15·35
Chlorine	2·73
Potassic oxide	15·95
Sodic oxide	4·62
Calcic oxide	21·70
Magnesic oxide	3·90
Ferric oxide	0·96
Aluminic oxide	0·31
Manganic oxide	0·16
Ignition	2·61
	100·71

"This ash is very anomalous in its composition as well as in the quantity present in the plants. The plants were not evenly matured at the time of gathering, and were in bad condition. The question we endeavoured to investigate, however, is perfectly answered by the results, *i.e.*, the oat plant can use the finely-divided felspar as a source from which to obtain potash, for in this experiment, made under very adverse conditions, we found that the oat plants took from the felspar 1·4417 grms. of potash. The potash added in the seed has been deducted. The silicic acid appropriated by the plant indicates the decomposition of the silicate."

In 1905 Prianischnikow, a Russian investigator, published the results of a series of pot tests using felspar and mica as sources of potash (*Landw. Vers. Stat.*, 1905, lxiii., 151). The felspar used was ground so that it was less than 0·25 mm. in diameter, corresponding to an 80-mesh sieve. The material was mixed with sand, and the other foods added in the form of phosphates and nitrates of lime and soda. The cultures used were tobacco, buckwheat, flax, peas, sunflowers, and barley. The tabulated results are too voluminous for insertion here, but they appear to show that the felspar, even in large amounts, had little or no effect on the growth of the plants. The investigator concluded that mica is, if anything, a better source of potash than felspar, but that neither of these minerals supplies a sufficient quantity to make them worth the slighest consideration so far as plant growth is concerned. The only criticism of these experiments that might be offered is that 80-mesh felspar powder is far too coarse to be used in pot experiments. This point will be taken up more fully later on.

The most important researches which have ever been published tending to show that under certain conditions finely-ground felspar is worthless as a fertiliser are those of von Feilitzen (U.S. Dept. Agriculture, *Ex. Sta. Record*, 1904, xvi., 30). This experimenter, like Nilson, worked on Swedish moor soils. He concluded that ground felspar is almost worthless as a fertiliser. The results and conclusions are best shown by abstracting from a translation from von Feilitzen's publications ("How Deficiency in Potash Affects Clover and Timothy"):—

"Potash, as is well known, is one of the necessary constituents of plant food; consequently, if it is absent in the soil or only there in insufficient quantities, a normal development of the higher orders of plants is not possible. According to the researches of plant physiologists, it is particularly instrumental in the formation and transport of the carbohydrates (sugar, starch, &c.), for which reason potash plays such a prominent part in the manuring of potatoes, turnips, and other root crops, but it is also required for cereals and all the other cultivated plants. Of late, comprehensive experiments have been carried out by Prof. Dr. H. Wilfarth at the experimental station at Bernburg, with the view to ascertain in what way the want of one or several of the necessary constituents of plant food influenced the development and appearance of plants. On this occasion he found that the want of potash caused a defective growth of some of the vegetative parts, the leaves of potatoes, tobacco, buckwheat, and beetroots assuming a speckled appearance (*Journ. für Landw.*, 1903, No. 11). Certain clearly defined portions, especially at the borders of the leaves, grew yellowish white and decayed, while the other parts retained their original appearance. These marks are often very much like those caused by fungi and insects, but if examined more closely it becomes evident that they cannot be due to such causes.

"In 1903 we made quite similar observations, when experimenting with clover and timothy grass, and, as it should be of interest, I shall describe in short the observations made by us. In 1902 a series of experiments were prepared in plots of soil of 1 square metre each (about 1 yard square), charged with rather well-decayed reed grass turf, poor in potash, in order to investigate whether the potash in a mineral fertiliser, prepared in Sweden, was of any manurial value. As, by analysis, this fertiliser turned out to be finely-ground felspar, we were prepared for an unfavourable result at the very outset."

The fineness of the ground felspar is not given, but an analysis showed that it contained 8·15 per cent of potash. The experimental series was made up of two plats, each fertilised as shown in the following table, and in May, 1902, they were sown with a clover-grass mixture containing red clover, bastard clover (alsike), white clover, and timothy grass. Even in the first year the grass developed vigorously, and produced vegetable matter, as shown in the table. An average of 1 square metre of each of the two parallel plats was taken. Fifty-four pounds of phosphoric acid were used on each plat.

Plat No.	Kind and quantity of fertiliser per acre.	Green vegetable matter produced (average of 2 plats). Pounds.	Increase due to potash (average of 2 plats). Pounds.
1.	Without potash and with 357 pounds of basic slag.. ..	1·20	—
2.	With 89 pounds of potash as potash manure salt	4·53	3·33
3.	With 89 pounds of potash as ground felspar	1·69	0·49
4.	With 178 pounds of potash as ground felspar	1·96	0·76

These figures show that this soil responded very well to the application of the soluble potash salts. While it must be admitted that the ground felspar was somewhat available, the effect appears to have been inconsiderable.

It is hard to reconcile such contradictory results as these which are given at length in the preceding pages. The only thing that can be said at the present time is that careful and systematic tests are required in order to determine finally to what extent and under what conditions ground felspar can be economically used in agriculture. The inference to be drawn would seem to be that under certain conditions finely-ground felspar is at least partially decomposed, so that its potash becomes sufficiently available to be made use of by certain crops. Under other conditions we are forced to the conclusion that ground felspar is of little value as a potash fertiliser.

Before proceeding with the description of experiments carried on by the Department of Agriculture it will be necessary to define, as briefly as possible, total and available potash, as the terms are commonly used. Potash is the name given to the oxide of the metallic element potassium. The name is derived from the fact that potash at one time was principally obtained by leaching wood ashes in large iron pots. The letter K is used by chemists as the symbol for potassium, the German name for which is Kalium. The oxide is written K_2O, which signifies that two atomic weights of potassium unite with one atomic weight of oxygen to form potash. Potash as such is a strongly caustic substance which unites with water to form a compound technically known as lye. Fertilisers, both natural and artificial, contain potash, invariably combined with some acid to form a compound or salt, such as sulphate, chloride, carbonate, nitrate, phosphate, or silicate. Although potash (K_2O) does not exist free in a fertiliser, the potassium present in whatever form is figured and reported as total potash (K_2O). Owing to the belief that has always been held by the majority of chemists and agriculturists that the potash combined as it is in the mineral silicates becomes soluble with extreme slowness, if at all, it is customary to distinguish between available and total potash. According to the official methods in vogue in this country the available potash is determined by boiling 10 grms. of the sample with 300 grms. of water thirty minutes, and analysing the water extract. In different places different methods are used; in some cases acid solutions are used to extract with, so that it is difficult to give an exact definition of available potash. However, it may be defined as all the potash that is present, in whatsoever form, which the crop can make use of in

one crop season. The text-book definitions, as well as the State fertiliser laws, are in need of revision in this particular respect. This is especially true in view of the fact that the value of a mixed fertiliser is figured, as far as potash is concerned, on the available or water-soluble potash alone. Even the potash contained in such organic fertilisers as cotton-seed meal and tobacco stems, which undoubtedly becomes available in one season, is not estimated as being available by the present methods of analysis, and therefore in many cases great injustice is done to manufacturers of mixed fertilisers, who should certainly be entitled to all the plant food contained in their mixtures which can be made use of by a crop in a single growing season.

Tobacco is particularly dependent upon abundant supplies of potash. In some of the tobacco-growing districts barnyard and stable manures are used, often enriched with an addition of commercial fertilisers. Since sulphates and muriates of potash are found to be harmful in certain ways to high grades of tobacco, the use of the strongly alkaline potassium carbonate has been largely resorted to on the tobacco crop. Potassium carbonate, which contains about 66 per cent of potash (K_2O), is an expensive compound, costing 90 to 95 dols. per ton, f.o.b. port of entry, or 6 to 7 cents per pound of unit potash. In addition to the cost of this salt, its strong alkalinity is an objectionable feature, and it is a grave question whether the annual addition to the land of a superabundance of such an alkaline salt will not be followed by an actually harmful effect. In view of the successful results which have attended the efforts of the Bureau of Plant Industry to improve the quality and yield of native tobacco by proper selection and breeding, it was decided to make a systematic investigation of the possible use of ground felspar as a potash fertiliser (see *Bull.* 96, Bureau of Plant Industry, U.S. Dept. of Agriculture; "Yearbook Dept. Agr.," 1905, p. 219).

Preliminary to the field and crop experiments which were to follow later, greenhouse experiments were begun early in the winter of 1905-6. Three large beds in the greenhouse, all having the same dimensions ($21\frac{1}{6}$ by $6\frac{2}{3}$ feet by 5 inches), were filled with a common unfertilised meadow soil taken from the surface after the removal of sod and grass roots. Four pounds of ground bone phosphate were broadcasted, and well worked in.

Bed No. 1 now received 2 pounds of potassium carbonate containing about 67 per cent of potash (K_2O). In order that the potassium carbonate might be evenly distributed, it was dissolved in 2 gallons of water, and sprinkled evenly over the bed. After drying out, the earth was again well worked.

Bed No. 2 received 17·4 pounds of finely-ground potter's felspar containing 8·3 per cent of potash (K_2O). This was also broadcasted, and well worked in. It will be seen that Beds 1 and 2 contained nearly equivalent amounts of potash, the only difference being that in one case the soluble carbonate was used and in the other ground rock.

No potash in any form was added to bed No. 3, which was used for comparison. The soil itself, however, contained about 0·5 per cent of total potash, and as the filtered Potomac River water which it was necessary to use for watering throughout the entire experiment contains an amount of potash equal to about 2 parts per million, the tobacco on bed No. 3 did not at any time show the effect of potash starvation.

All three beds were supplied with a sufficient quantity of nitrogen in the form of pure ammonium nitrate. The seed chosen for the experiments was carefully selected Cuban wrapper tobacco. In making experiments of this kind it is necessary to select seedlings as nearly as possible of equal vigour. It is not improbable that many wrong deductions have been drawn from pot or plat experiments in which the need for careful selection of seed has been overlooked.

Tobacco seedlings were set out in four rows of ten plants each in the three beds. The tobacco crop is usually planted with about 8000 plants to the acre, so that the experimental plats represented, as far as plant growth was concerned, one two-hundredth of an acre. The actual amount of potash added to plats Nos. 1 and 2 was equivalent to 280 pounds to the acre. As the original soil contained a sufficient amount of potash to mature some sort of a crop on plat No. 3, it is not possible to state the actual amount of potash present in the three plats. The potash in the soil was not water-soluble, and would not have been termed available in the present sense of the word.

The tobacco grew well throughout the experiment, and for the first six weeks very little difference was noted. After this time, however, it became evident that the plants in plat No. 3 were falling behind. At the end of twelve weeks the plants in plat No. 3 were plainly stunted and much less developed than those in the other two plats. The tobacco grown in plats Nos. 1 and 2 was evenly developed, fully matured, and of a good quality. It was carefully harvested in the usual way, and the yield of green tobacco weighed. After curing, the actual yield of leaf was also recorded. The results, which are shown in the following table, appear to indicate that the felspar potash was available to quite the same extent as that which was added as potasium carbonate:—

TABLE III.—*Results of Greenhouse Experiments with Tobacco Plants.*

No. of Plat.	Source of potash.	Actual weight of green crop.	Estimated weight of green crop per acre.	Actual weight of cured leaf.	Estimated weight of cured leaf per acre.
		Pounds.	Pounds.	Pounds.	Pounds.
1.	Potassium carbonate	154·0	30,800	5·70	1140
2.	Ground felspar ..	155·0	31,000	6·30	1260
3.	—	128·5	25,700	5·30	1060

These yields do not in any case equal those obtained in the field under the best crop conditions, but for a winter greenhouse crop raised in shallow beds they are satisfactory.

On the completion of the greenhouse experiments arrangements were made to carry on field trials in Connecticut and Florida under standard crop conditions. In the tobacco-growing district of Connecticut it is customary to use from 150 to 250 pounds of carbonate of potash to the acre of tobacco. The co-operation of several prominent tobacco-growers was obtained, who each agreed to try an acre, substituting for the usual carbonate 1 ton of potter's spar, running 8·3 per cent of potash, or 186 pounds to the ton. The broadcasting and working in of the felspar was done under the personal supervision of representatives of the Department of Agriculture, and none of the experimental acres received any potash except that contained in the ground spar. All the experimental fields did as well as any in their neighbourhood, and matured excellent crops. The following letters were received from the growers themselves in regard to the use of felspar:—

Tariffville, Con., February 11, 1907.

Dear Sir,—In reply to your letter of February 5, I would say that I used the ton of finely-ground felspar as a potash fertiliser for tobacco, and used no other form of potash on the plat in connection with the felspar. This plat (one-half acre) was treated exactly like the rest of our tobacco lands as regards nitrogen, phosphoric acid, lime, &c.

We had a fine large growth of tobacco where the felspar was used; fully as large as any in our fields, and much larger than in some sections of our fields.

I do not consider this an absolute or hardly a fair test of the felspar, as it was used on land that had previously grown tobacco for several years, and each year we had fertilised heavily with carbonate of potash. I will be pleased to give you more detail if you wish.—Yours respectfully, J. S. DEWEY.

Hartford, Conn., February 7, 1907.

Dear Sir,—In reply to your letter of February 5 regarding the finely-ground spar, would say that we used this material as a potash fertiliser as directed by you last

spring. This was used on comparatively new land, tobacco having been grown only one season previous to this past season. During the growing season we could not see any perceptible difference on the same land between this tobacco and that treated with carbonate of potash, planted side by side. We hung this tobacco in the same shed, it being cut at the same time, where we were able to identify it after it was cured. We are glad to report that the tobacco grown where the ground felspar was used was exceptionally nice tobacco. It was so pronounced by tobacco experts who have examined it.

The tobacco grown on the same character of land beside where this was grown was exceptionally nice tobacco, but we think if there was any preference it would be for that grown on the felspar. It certainly was beautiful in every respect. We should be very glad to conduct an experiment on 1 acre or less on new land that has never grown crops of any kind or been fertilised in any way by stable manure or other fertiliser, and follow this up for, say, three years. We have a piece of land we think well adapted to make the experiment. The result this past year has been so gratifying that we would be very glad to carry it a little further, if possible.

Any further information we can give you we will be glad to furnish.—Yours truly, Olds and Whipple.

Suffield, Conn., February 16, 1907.

Dear Sir,—Yours received inquiring about the finely-ground felspar sent me. Would say that I used it on 1 acre of tobacco and got very satisfactory growth. The only difference I could detect in tobacco grown on this acre and the adjoining land, where I used cotton-hull ashes for potash, was that the burn of the tobacco grown on the latter was not quite as clear as that of the tobacco grown on the felspar.—Yours respectfully, Edmund Halladay.

Quincy, Fla., March 7, 1907.

Dear Sir,—In reply to your favour, I beg to state that 1 acre of tobacco was grown here last year on ground felspar, and as far as we were able to tell from the appearance of the tobacco in the field the growth was equally as good as where other forms of potash were used. Mr. Underhill, who used this felspar, was not able to harvest the tobacco separately on account of scarcity of labour in harvest season.

I am planting some plat experiments this year in which I have included the ground felspar, to be compared with other forms of potash, and hope to get some information in this way. In addition to this I shall put out at least 2 acres of felspar as a substitute for carbonate of potash, and will report results at the end of the season. —Yours very truly, W. W. Cobey.

Although it is admitted that these experiments have not as yet proved the value of ground felspar for tobacco, it is quite certain that the experimental crops found all the potash they required. If we assume that von Feilitzen and others are right, and that the felspar is of little or no value, we must conclude that the practice of adding potassium carbonate each year to the tobacco fields is unnecessary.

Many attempts have been made by the writer to devise crucial tests which would show decisively whether or not the ground felspar is actually capable of giving up potash to growing plants. One of these experiments, which was undertaken in co-operation with Dr. L. J. Briggs, of the Bureau of Plant Industry, is interesting on account of its direct bearing on this point. A wooden trough of 1 square foot cross-sectional area and 30 feet in length was filled with a poor meadow soil, containing no appreciable quantity of water-soluble potash. About 5 pounds of fine-ground felspar, containing 9·3 per cent of total potash, was then evenly distributed over the surface of the trough, and well worked into the soil. Carbon electrodes of about 1 square foot area were inserted at the extreme ends, and tobacco seedlings set out at 1-foot intervals along the trough. The carbon electrodes were connected to a 110-volt direct-current lighting circuit, and a current of electricity was passed continuously in the same direction through the soil while the growth of the plants was in progress. The amount of current varied with the moisture content of the soil—between the limits of 5 and 15 milli-ampères. The plants made a flourishing growth, and at the end of several weeks it was apparent that the best growth was being made in the neighbourhood of the centre of the trough, the plants at the extreme positive and negative ends being more or less stunted. The soil at the beginning of the experiment was neutral to litmus-paper. At the end of the experiment, when the plants had attained a maximum height of 2 feet, a sample taken from the positive end of the trough reddened litmus-paper, showing it to be decidedly acid. The middle section by the same test was shown to be faintly and the negative end strongly alkaline. While no sweeping deductions can be drawn from the single experiment, it is quite certain that a partial transference of the alkaline bases from the positive to the negative end of the trough had occurred. This effect could only take place with that portion of the bases which had actually passed into solution. The results of this experiment appear sufficiently interesting to warrant repetition under still more careful conditions.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

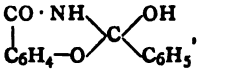
The following are abstracts of Papers received during the vacation, and published or passed for publication in the *Transactions*:—

162. "*Studies in the Barbituric Acid Series.* I. 1 : 3-*Diphenylbarbituric Acid and some Coloured Derivatives.*" By Martha Annie Whiteley. (*Trans.*, 1907, 1330).

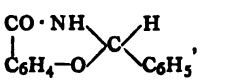
In addition to the coloured derivatives of 1 : 3-diphenylbarbituric acid already described (*Proc.*, 1006, xxii., 200; 1907, xxiii., 180), 1 : 3-*diphenyl*-5-*diphenylmethylenebarbituric acid*, $CO<^{NPh\cdot CO}_{NPh\cdot CO}>C:CPh_2$, was prepared from 1 : 3-diphenylbarbituric acid and benzophenone dichloride; it forms yellow prisms melting at 264°, and, like the similarly constituted benzylidene derivative, yields a colourless acid, 1 : 3-*diphenyl*-5-*diphenylmethylbarbituric acid*, $CO<^{NPh\cdot CO}_{NPh\cdot CO}>CH\cdot CHPh_2$, m. p. 205—206°, on reduction.

163. "*Phenylbenzometoxazone and Related Derivatives.*" By Arthur Walsh Titherley. (*Trans.*, 1907, 1419).

According to McConnan and Titherley (*Trans.*, 1906, lxxxix., 1318), O- and N-acylsalicylamides are labile and mutually transformable through an intermediate cyclic metoxazone structure. The alternative tautomeric formula for N-benzoylsalicylamide is—



and the related compound, phenylbenzometoxazone,—



has been isolated by the condensation of salicylamide and benzaldehyde by means of alcoholic hydrogen chloride (compare Keane and Nicholls, *Trans.*, 1907, xci., 266). The relation between phenylbenzometoxazone and N-benzoylsalicylamide is confirmed by the fact that the former passes into the latter on careful oxidation. When salicylamide and benzaldehyde condense in presence of

anhydrous sodium acetate, benzylidenesalicylamide results as well as phenylbenzometoxazone :—

$$C_6H_4\!<\!\begin{matrix}CO\cdot NH_2\\OH\end{matrix} + C_6H_5\cdot CHO \rightarrow$$

$$\rightarrow C_6H_4\!<\!\begin{matrix}CO\cdot N{:}CH\cdot C_6H_5\\OH\end{matrix}.$$

An isomeric benzylidenesalicylamide has also been obtained by rearrangement of phenylbenzometoxazone with pyridine and alkali. The two isomerides are amorphous and similar in physical properties, but differ markedly in stability; that produced by condensation is stable, but the other, derived from phenylbenzometazone, rearranges completely into this compound on melting. The two benzylidenesalicylamides are probably geometrical isomerides :—

$OH\cdot C_6H_4\cdot CO\cdot N$
$\quad\quad\quad

Dunstan (*Trans.*, 1904, lxxxv., 817; 1905, lxxxvii., 11; 1907, xci., 83) to solutions of pyridine, α- and β-picoline, and 2:6-lutidine in various solvents. These bases in aqueous solution give curves which exhibit maxima, the discontinuities being at points of simple molecular concentration. These maxima are attributed to the addition of the elements of water at the nitrogen atom of the pyridine, or its homologues.

170. "*The Atomic Volumes of Phosphorus.*" By EDMUND BRYDGES RUDHALL PRIDEAUX. (*Trans.*, 1907, 1711).

The author has determined the coefficients of expansion of phosphorus and phosphorus pentachloride, and has calculated the values of the constants from the equations $V_t = V_0(1+at+\beta t^2)$, expressing the expansion of phosphorus between 60° and 235°, and $V_t = V_0(1+at)$, expressing the expansion of phosphorus pentachloride between 160° and 190°. From these equations, values are obtained for the specific volumes of phosphorus and phosphorus pentachloride at their respective boiling-points.

The atomic volume of quinquivalent phosphorus can thus be compared with those of tervalent and elementary phorphorus.

171. "*The Action of Potassium Sulphite on Potassium Tetrathionate in Aqueous Solution.*" By ARTHUR COLEFAX.

By the joint estimation of the iodine titration and the acidity developed in the solution when the iodine titration is completed, the nature of the interaction of potassium sulphite and tetrathionate in aqueous solution has been investigated.

If potassium sulphite and tetrathionate react in equimolecular proportions in aqueous solution, the conversion of sulphite into thiosulphate and consequent formation of trithionate which occurs does not proceed to completion, and pentathionate is not permanently formed in the solution. If the relative proportions in which these bodies are originally present in the solution are either $K_2SO_3 : \frac{1}{2}K_2S_4O_6$, or $K_2SO_3 : 2K_2S_4O_6$, the theoretically complete conversion of sulphite into thiosulphate takes place. In the latter case, where the proportions are $K_2SO_3 : 2K_2S_4O_6$ when the sulphite has been completely converted into thiosulphate, pentathionate is found in the solution in considerable amount.

Certain preliminary experiments established that—(*a*) Potassium sulphite and trithionate do not react in aqueous solution; (*b*) potassium thiosulphate and tetrathionate react in aqueous solution to form pentathionate, the resulting sulphite being immediately re-converted into thiosulphate; (*c*) potassium thiosulphate and trithionate react in aqueous solution, although to an extremely small extent; and (*d*) potassium sulphite rapidly abstracts sulphur from pentathionate when the two salts react in aqueous solution.

172. "*The Adsorption of Iodine by Carbon.*" By OLIVER CHARLES MINTY DAVIS. (*Trans.*, 1907, 1666.)

An investigation has been carried out on the adsorption of iodine dissolved in various organic solvents, by means of animal, sugar, and cocoanut charcoal.

The main objects of the research were to investigate the effect of temperature and time on the amount of adsorption, and to compare the adsorbing values of the three forms of carbon.

The effect of temperature was found to be very small, but that of time was well marked.

The experiments demonstrate the fact that adsorption, although rapid at first, proceeds slowly for lengthened periods after a "surface equilibrium" has been maintained, proving that both surface action and diffusion are concerned in the mechanism of adsorption.

The adsorbing values of animal and sugar carbon are roughly the same, whilst that of cocoanut carbon is much less than these.

173. *Adsorption Formulæ.*" By JAMES WILLIAM MCBAIN. (*Trans.*, 1907, 1683.)

The results of recent work on absorption have been expressed by either of the following two formulæ, which are applicable to gases or solutions:—

$$\frac{x}{m} = \beta c^{1/p} = \beta\left(\frac{a-x}{v}\right)^{1/p} \quad \text{I.}$$

$$\lambda = \frac{v}{m} ln \frac{a}{a-x} = \alpha\left(\frac{a}{v}\right)^{-1/n} \quad \text{II.}$$

where x is the amount of substance adsorbed, a is the total amount of that substance, $\frac{a-x}{v} = c$ its concentration in the fluid phase, m the weight of adsorbing substance, and λ, β, α, p, and n are constants.

There are, however, some very serious disadvantages inherent in the use of the λ-formula, whereby an equilibrium is referred to a parameter a/v with which it has no apparent connection. This expression, introduced to represent the amount of adsorption, does not lead to any definite number characteristic of each set of substances, and, moreover, its results are irreconcilable with each other and with experiment.

174. "*The Diazo-derivatives of Benzenesulphonylbenzidine.*" By GILBERT T. MORGAN and JAMES MORTON HIRD. (*Trans.*, 1907, 1505.)

Benzenesulphonylbenzidine and as-*benzenesulphonylmethylbenzidine*, $C_6H_5{\cdot}SO_2{\cdot}N(CH_3){\cdot}C_6H_4{\cdot}C_6CH_4{\cdot}NH_2$, give rise to stable, coloured diazonium salts; those derived from the latter base are of interest in connection with the formulæ recently put forward for diazonium derivatives, because they show that the presence of a labile hydrogen atom is not necessary for the development of colour in this series of substances.

175. "*The Interactions of Aromatic Amines and Paradiazoimides.*" By GILBERT T. MORGAN and FRANCES M. G. MICKLETHWAIT. (*Trans.*, 1907, 1512.)

The para-diazoimides recently described by the authors combine additively with the more reactive aromatic amines to give rise to aminoazo-compounds.

This combination occurs in some instances when the reagents are intimately mixed in the dry state, the reaction being accelerated by the addition of a small amount of pyridine. Benzenesulphonyl-*p*-phenylenediazoimide combines in this way with α- and β-napthylamines and certain of their derivatives, but the reaction does not take place with aniline and its homologues.

176. "*Molecular Aggregation in Solution as Exemplified in Aqueous Mixtures of Sulphuric Acid with Inorganic Sulphates.*" By JOHN HOLMES and PHILIP JOHN SAGEMAN. (*Trans.*, 1907, 1606.)

The authors have determined the volumetric data of a series of mixtures of dilute sulphuric acid with aqueous solutions of neutral inorganic sulphates. In all cases, the volume of the mixture was found to be greater than the sum of the initial volumes.

From a consideration of the results obtained, the authors conclude that the volumetric changes are due to physical forces inherent to the molecules, and this theory is supported by a comparison with the results obtained in mixtures in which chemical change is known to occur.

By elimination of extraneous influences due to the solution medium, the relative aggregations of the interacting molecules can be determined.

177. *The Wandering of Bromine in the Chlorination of Bromoanilines.*" By WALTER WILLIAM REED and KENNEDY JOSEPH PREVITÉ ORTON. (*Trans.*, 1907, 1543.)

When *p*-bromoaniline is directly chlorinated, the normal product, 2:6-dichloro-4-bromoaniline, is not alone formed. Partial displacement of the bromine by the chlorine takes place, and a mixture of chlorodibromo-, dichlorobromo-, and *s*-trichloro-anilines results, which cannot be resolved into its constituents. Such a reaction does not occur only when excess of chlorine is used, but also with the calculated quantity of the reagent. The solvent has little effect, the same mixture being obtained when 20 per cent

hydrochloric acid or such anhydrous solvents as benzene, chloroform, or carbon tetrachloride are employed. Similar results were observed on treatment of 2 : 4-dibromoaniline with one molecular proportion of chlorine, *s*-tribromoaniline being among the products of the change. *o*-Bromo-, *m*-bromo-, and 2 : 6-dibromo-aniline, on the other hand, yield respectively only a single chlorinated product.

2 : 6-Dichorobromoaniline can be obtained indirectly by two methods, either by molecular rearrangement of acetyl-chloroamino-2-chloro-4-bromobenzene which yields the acetyl derivative of the aniline, or by the action of acetyl-chloroamino-2 : 4-dichlorobenzene on *p*-bromoaniline, when 2 : 4-dichloroacetanilide and 2 : 6-dichloro-4-bromoaniline are formed :—

$$C_6H_4Br\cdot NH_2 + 2C_6H_3Cl_2\cdot NClAc = C_6H_2Cl_2Br\cdot NH_2 + 2C_6H_3Cl_2\cdot NHAc.$$

(To be continued).

PHYSICAL SOCIETY.

Ordinary Meeting, October 25th, 1907.

Prof. J. PERRY, F.R.S., President, in the Chair.

A PAPER by Dr. J. A. FLEMING, F.R.S., on "*Magnetic Oscillators as Radiators in Wireless Telegraphy*," was read by the author.

An open or Hertzian oscillator is called an electric oscillator because the effects produced in space are due in part to the potential of the free charges at the ends. A closed circuit oscillator is called a magnetic oscillator because the effects it produces are wholly due to current. Hertz showed that the energy radiated per period from an open oscillator could be expressed by the formula $E = 16\pi^4\phi^2/3\lambda^3$, where λ is the wave-length and ϕ the electric moment. The author has shown that a similar formula $E = 16\pi^4 M^2/3\lambda^3$, where M is the magnetic moment, holds good for the closed circuit oscillator. Assuming persistent or undamped oscillations to be used, these formulæ were transformed by the author into two others, viz. :—$W = 87 \times 10^{-30} l^2 a^2 N^2$ for the open oscillator, and $W = 4 \times 10^{-28} S^2 a^2 N^2$ for the closed oscillator, where *a* is the R.M.S. value of the current in the oscillator and N is the frequency. Hence the radiation from the open oscillator varies as the square of the frequency, and that from the closed one as the fourth power. The paper describes experiments made with flat square coils of various sizes used as magnetic oscillators in the quadrangle of University College, London. In one circuit undamped oscillation were set up by means of a Poulsen arc, and the induced oscillations created in the other circuit at a distance were detected and measured by means of the author's oscillation valve or glow-lamp detector. The distance separating the two circuits was varied from about 50 to 250 feet. Curves were obtained showing how the secondary current varied with the distance of the circuits apart and with their relative position. It was shown that the inductive effect was greatest when the flat coils were in a horizontal position and at a certain distance above the earth.

The law of variation with distance proved to be something between the inverse cube and the inverse square of the distance. It was then shown that increase in size of the coils had a very marked action in increasing the inductive effect, and also that for equal power the use of the spark method creating intermittent oscillations in the primary gave better effects than the use of the arc or undamped oscillations.

It was also shown that for the coils used the true radiation of energy was very small, and therefore that the distance effects obtained were almost entirely due to magnetic or faradaic induction.

Suggestions were then made for increasing the efficacy of the ordinary inductive type of wireless telegraphy by the use of high frequency oscillations in the primary circuit, and a suitable detector such as the author's oscillation valve combined with a telephone as a receiver in the secondary circuit. Such a method would have a far greater reach than the ordinary low-frequency alternating current inductive telegraphy and not be open to the objection of disturbing commercial telephonic circuits.

Mr. A. RUSSELL thanked the author for his clear exposition of the theory of electric oscillators and for the valuable formulæ he gave for magnetic oscillators. The experiments described were exceedingly interesting and instructive. It was, however, difficult to interpret some of the results obtained. He asked whether the author had been able to find a position for the secondary coil in which no current was induced in it. Possibly buried pipes or metallic conductors, iron girders in adjacent buildings, or iron railings in the neighbourhood, might have had some influence in modifying the inductive effects between the coils.

Mr. TAYLOR said that the Post Office had tried arrangements similar to those described for magnetic space telegraphy, and had found that the closed circuit method was inferior to that in which earth-connected vertical coils were used. The ratio between the received currents when using an earth-connected and a closed circuit was often as great as eighty to one, and he thought the improvements in the closed-circuit method would have to be very great to make it equivalent to the earthed-circuit method.

A paper "*On the Use of Variable Mutual Inductances*" was read by Mr. A. CAMPBELL.

In connection with wireless telegraphy the measurement of small inductancss and capacities is of importance; one of the methods described has special reference to small self-inductances. Mutual inductances can be more easily dealt with than self-inductances, for the former can be (1) more accurately calculated from dimensions, (2) are less affected by change of frequency, and (3) when variable can be made to pass through zero value. A convenient form of variable mutual inductance consists of a continuously variable part and a series of steps. The first consists of two equal parallel coils with a third coil moving parallel to their planes round an axis eccentric to the fixed coils. The scale thus obtained is very open near zero (which is an advantage) and the graduation is done by experiment, a theoretical discussion being given in an appendix. The steps are obtained by means of another fixed coil of stranded wire, each strand giving an equal subdivision. The model shown had two ranges, from 0·01 up to 200 and 2000 microhenries. A variable mutual inductance of this type has a number of applications. It is obviously convenient for calibrating ballistic galvanometers. By means of it mutual inductances of all values can be readily measured. By several methods it can be used to measure capacities, and the formulæ required are mostly very simple. Its most important application, however, appears to be to the measurement of small self-inductances as follows :—Let the variable mutual inductance be called W. With a source of intermittent or alternating current and any convenient detector (vibration galvanometer, telephone, &c.) a bridge with corners A, B, C, D is formed, in which BD and DC are equal non-inductive arms, AB is the fixed secondary of W, and AC has resistance and self-inductance equal to those in AB. The detector is across BD, while the source is applied at D and also through the primary of W connected to A. When W is set to zero reading a balance is obtained. An unknown small self-inductance N is now inserted in AC, and the balance restored by adding resistance in AB and adjusting the mutual inductance W. The reading of W when doubled gives directly the value of the unknown N. The method is really a differential one and can also be used to give very accurate measurements of the difference between two nearly equal large self-inductances.

The discussion on Mr. Campbell's paper was postponed until the next meeting.

NOTICES OF BOOKS.

A Scheme for the Detection of the more Common Classes of Carbon Compounds. By FRANK E. WESTON, B.Sc. (Lond.), F.C.S. New Edition. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1907.

THE second edition of this book has been considerably enlarged, and its size is now almost twice that of the first edition, issued three years ago. The new matter, which accounts for this extra bulk, is of considerable importance, and although the beginner will now find that there is much which is beyond his requirements, the usefulness of the book for Honours students is considerably increased. The greater part of the additional matter deals with the identification of individual members of groups, and when the student has discovered, for instance, that the substance he has to identify is a phenol, he will no longer have to look up in his text-book the information which will enable him to decide what particular phenol it is—he will find full enough details of the chemical and physical properties of the more common members of the class to proceed to the identification of the individual. Fuller information is also given with regard to the experimental arrangement of some of the tests, and several new methods, which have been perfected since the appearance of the first edition, are now included. The book will be found a valuable aid in systematising the students' practical work in organic chemistry, and giving him a grasp of the chief reactions of all the more important classes of carbon compounds, and is specially suitable for the use of candidates for the London B.Sc. and the Honours Chemistry Examination of the Board of Education.

Fire Tests with Petrol Tanks. (Henze Patents). London: The British Fire Prevention Committee. 1907.

THE results of fire tests with tanks containing petrol and other inflammable liquids, and fitted with patent safety devices, are described in this pamphlet. The special appliances employed include a safety plug, and an interior safety wire-gauze tube, the patents of which have recently been acquired by the Safety Non-Explosive Reservoir Company, Ltd. The tanks and vessels were subjected to severe tests in order to prove the efficiency of the devices, and the results appear to show that the inventions are of great value as a safeguard against explosion. The safety plug prevents the bursting of the vessels, even when a bonfire is lit beneath them, the escaping vapour merely burning quietly at the mouth, and if the safety gauze tube is fitted into the interior there appears to be practically no danger of the vapour igniting inside the vessel.

E. Merck's Annual Reports. Vol. XX. Darmstadt: E. Merck. 1907.

THIS volume of annual reports gives a brief review of all the novelties which have come into use in therapeutics during the last twelve months. Statistics concerning the doses and use of new drugs are given, and notes upon the results obtained with them, and also upon the adoption of well-known preparations in diseases for which they have not hitherto been recommended. A bibliographical index gives a list of publications upon therapeutical and pharmaceutical subjects which appeared in 1906, and a table is added showing the approximate prices of all the preparations mentioned in the reports. The book will be sent free to medical men and others interested in pharmacology and therapeutics, on application to the London office at 16, Jewry Street, E.C.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 4th inst., Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. Sir R. J. Collie, Sir Murland Evans, Bart., and Mr. H. Richardson were elected Members.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlv., No. 16, October 14, 1907.

Analysis of Mixtures of Air and Combustible Gases and Vapours.—Jean Meunier.—With ordinary measuring cylinders of fixed volume the proportions of the mixtures used can only be multiples of the volume given by the pipette, and it is impossible to weigh the gas for analysis. The author's improved apparatus for the purpose consists of a measuring cylinder graduated in cubic centimetres and closed at the bottom by a movable copper piston on which some mercury is poured. The upper end of the cylinder is somewhat constricted, and can be closed by a glass cap with a cock through which the gases to be investigated can be introduced. A known weight of volatile liquid is put into the measuring cylinder by means of a pipette, and by adjusting the piston a given weight of gas can be made to occupy any desired volume.

A New Method of Rapidly Determining Methane.—Nestor Gréhant.—The author finds that, when an electric current passes along a red-hot platinum wire in mixtures of air and methane, incomplete combustion is produced unless the current is passed from two hundred to four hundred times, or even more. The figures he has obtained show, moreover, that, in his eudiometer, methane can be estimated rapidly and with a sufficient degree of accuracy for most practical purposes.

Vinylic Alcohol of the Type ArR = C = CHOH.—MM. Tiffeneau and Daufresne.—No secondary vinylic alcohol has yet been isolated, and it has hitherto generally been believed that vinylic alcohols are incapable of existing in the free state. When, however, dry potassium acetate in alcoholic solution and alcoholic potash are allowed to act in succession upon the dibromide of $OCH_3—C_6H_4—CH_2—CH_2—CH_3$, the following reaction takes place:—

$$OCH_3—C_6H_4—CH_2—CHBr—CH_2Br \rightarrow OCH_3—C_6H_4—C(CH_3)=CHOH.$$

The product, formerly supposed to be anisylcyclopropanol, has now been shown by the authors to be a true vinylic alcohol, methylanisyl ethanol. It is stable in neutral or alkaline media, and is the first representative of the class which has been prepared.

Reactions of Nickel-plating Bath.—A. Brochet.—The deposition of nickel must be carried out in a neutral bath; in a slightly acid solution gas is evolved and the metal rises in the form of scales. In presence of sulphates sulphuric acid is set free and oxygen evolved. The presence of alkaline salts is essential in order that nickel may be satisfactorily deposited; ammonium salts are the best to employ. They give with nickel sulphate complex salts which dissociate into cations, NH_4, and anions, $(SO_4)_2Ni$, and these latter have their charge neutralised by that of the Ni ions furnished by the anode. Nickel sulphate is formed and also oxygen and sulphuric acid. Nickel peroxide also results, owing to the intermediate formation of unstable nickelic sulphate. These reactions are not modified by the addition of chlorides; a precipitate of hydrate of nickel oxide is formed and is deposited at the same time as the nickel. In order to prevent the bath becoming acid it is best to add salts which do not easily dissociate, and also to add boric acid in order to make the deposit white.

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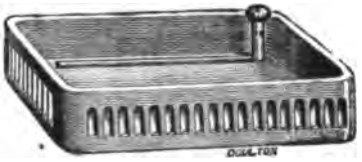

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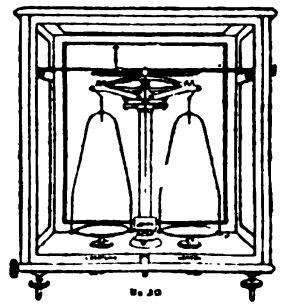

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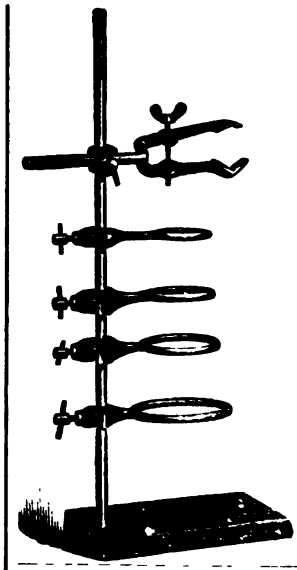

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VULCANISATION TESTS WITH PLANTATION RUBBER.

(THIRD COMMUNICATION).

By CLAYTON BEADLE and HENRY P. STEVENS.

Specific Gravity of Vulcanised but Unloaded Rubbers.

In previous communications to the CHEMICAL NEWS (vol. xcvi., pp. 37 and 187) we have described the results of a number of vulcanisation tests on high-grade plantation rubbers and also on hard-cure para. The vulcanisations were carried out in our laboratories on mixings consisting of caoutchouc and sulphur only, the proportion of the latter being usually 6 per cent, although mixings were also vulcanised containing 5 per cent and 8 per cent of sulphur. The vulcanised samples were then tested and the tensile strength and elongation recorded.

With a view to carrying our investigations a step further, we have determined the apparent specific gravity of the vulcanised samples and subjected our figures to a close examination, with a view to finding some relation between the specific gravity and conditions under which the samples were vulcanised, if such should exist.

In a great number of cases, owing to the simultaneous variation both in temperature (or pressure) and time of vulcanisation, it is not possible to make a direct comparison, although in some of these cases the tensile strength and elongation affords some clue. Unfortunately, the specific gravity of many samples was not taken till many months after they had been prepared, and the results are vitiated by the tendency of the specific gravity to increase on keeping, especially in the case of fully cured samples.

In this respect, the over-cured samples which had been kept many months showed comparatively high specific gravities, and a loss in tensile strength was generally accompanied with a marked increase in specific gravity, and both plantation rubbers and hard-cure para showed substantially the same behaviour.

Turning now to the recently vulcanised samples, the following figures illustrate the variation in specific gravity with the cure.

Mixing D_3 consisted of hard-cure para with 6 per cent of sulphur; O_3, a plantation rubber (block) with 8 per cent of sulphur; and V_2, another plantation rubber (biscuit) with 6 per cent of sulphur.

TABLE III.

		Length of cure (hours).	Apparent specific gravity.
D_3	270	3	0·9489
	266	4	0·9565
	260	5	0·9582
	257	6	0·9566
O_3	297	2	0·9517
	299	2½	0·9534
	295	2½	0·9567
V_2	271	3	0·9579
	264	4	0·9560
	258	5	0·9564
	255	6	0·9462

In many cases the specific gravities of a series of cures made on one mixing give figures differing but little from one another.

Mixing O_2 consisted of plantation rubber (block); Q_2, hard-cure para; P_2, hard-cure para; and R_2, plantation rubber (biscuit). All with 6 per cent of sulphur.

TABLE IV.

	O_2.	P_2.	Q_2.	R_2.
	0·9429	0·9464	0·9554	0·9412
	0·9494	0·9387	0·9454	0·9492
	0·9429	0·9450	0·9456	0·9496
	0·9474	0·9459	0·9476	0·9484
	0·9474	0·9444	0·9522	0·9474
	0·9454	—	0·9530	—
	0·9449	—	0·9472	—
	0·9479	—	—	—
Mean	0·9460	0·9444	0·9495	0·9471

In spite of the fact that many of these were under-cured and some over-cured, the specific gravities, taken a few weeks after they were made, revealed the fact that the differences are very small. Moreover, it is noteworthy that two totally different types of plantation rubber, as block and biscuit, one from Malay and the other from Ceylon, and hard-cure para from the Amazon, all three prepared in different ways, gave results practically identical with one another.

A very large number of specific gravity determinations have been made, but no object would be gained by giving them in detail, as they would not serve any useful purpose. As a general rule, the specific gravity does not fall below 0·94 and seldom reaches 0·96, except in samples which have been over-cured and kept some months, when they usually exceed 0·96 or even reach 0·98 in samples containing 6 per cent of sulphur.

Portions of the vulcanised samples which had been used for determination of tensile strength, and which had been put aside for a short time, gave the same figures for specific gravity as pieces of the same sample which had not been subjected to distortion. On the other hand, if examined immediately after testing, the sample showed a lower specific gravity than an untreated portion of the same sample.

Tests with Ceylon Biscuit Rubber.

In extending our researches on vulcanising rubber in other directions, we have made up a few mixings and carried out a number of vulcanisation tests with Ceylon biscuit rubber. This biscuit was the best obtainable, and on analysis showed a very high percentage of caoutchouc.

TABLE V.—*Ceylon Biscuit.*

Moisture	0·5
Albumenoids	0·1
Resin	2·8
Ash	0·4
Caoutchouc (by difference)	96·2

The results of the tests are given in Table VI.

TABLE VI.

Vulcanisation reference number.		Tensile strength, in grms.	Elongation at rupture when original = 1·0.	Elongation under a strain 1500 grms. when original = 1·0.
212		548	6·9	—
217		1720	13·0	12·4
215	R_2	2352	13·6	13·0
226		2634	13·4	10·8
223		2331	11·4	8·9
231		2280	14·7	12·9
249		2436	13·5	12·5
234		2513	14·5	11·7
271	V_2	1472	12·0	11·3 (*a*)
264		2639	13·0	10·1 (*b*)
258		2645	13·0	9·8 (*c*)
255		Very short and weak.		(*d*)

Duration of vulcanisation: (*a*) Three hours, (*b*) four hours, (*c*) five hours, (*d*) six hours.

As far as possible the vulcanisations are arranged in order of duration and temperature, starting with the shortest and ending with the longest cure. In the case, however, of vulcanisations V_2 271, 264, 258, 255 a close comparison is possible, as the temperature of vulcanising was in all cases the same. V_2 271 is obviously undercured; it shows an elongation of 11·3 under a load of 1500 grms. On giving this mixing four hours' treatment instead of three, the tensile strength rises practically to the maximum, the elongation being reduced from 11·3 to 10·1. On giving the mixing still another hour's vulcanisation the tensile strength is not materially increased, while the elongation is reduced to 9·8. On vulcanising for six hours a very short and brittle product was obtained, which was so weak that it did not appear worth while to test it. V_2 255 is therefore considerably over-vulcanised, and V_2 258 is also probably vulcanised longer than is needful.

As we are only able to record the results of vulcanisation tests on two mixings with Ceylon biscuit, we should hesitate to draw too positive a conclusion from the results of our tests. On the whole, the tensile strengths, when averaged up, are not very different from the figure obtained in the case of hard-cure para, and there is not much to choose between them. On the other hand, taken in conjunction with the tests on vulcanised block rubber published in our previous communication, it is obvious that the samples of block we have examined yield a vulcanised product of greater tensile strength than the sample of Ceylon biscuit.

While not desiring to push this conclusion too far, we must admit that the tests with Ceylon biscuit were made on samples from one plantation only; yet it is not likely that other samples of biscuit would yield better results, as we chose for purposes of our experiments one of the highest quality biscuit to be found on the market.

THE COMBUSTION OF SULPHUR IN AIR AND OXYGEN.

By J. H. KASTLE and J. S. McHARGUE.

SULPHUR dioxide has long been employed as a disinfectant and germicide. For many purposes it is regarded as highly efficient and in general its mode of action is sufficiently well understood. Like other substances employed for purposes of disinfection its efficiency is dependent on various conditions such as temperature, moisture, &c., and to some of these its relation is still not well understood. An experimental study of its mode of action as a germicide has therefore been recently undertaken in the Hygienic Laboratory of the U.S. Public Health and Marine Hospital Service, and the observations herein described were made in connection with this investigation. Ordinarily, the sulphur dioxide required for disinfection is obtained by burning sulphur in air in pots or furnaces, the latter specially designed for this purpose. It therefore became a matter of interest in this connection to determine whether sulphur dioxide is the sole product of the combustion of sulphur, and especially to determine whether any sulphur trioxide is formed during the combustion.

According to Hempel (*Ber.*, xxiii., 1455), when sulphur is burned in oxygen the quantity of sulphur trioxide produced increases with increase in the pressure of the oxygen to 40 to 50 atmospheres, when approximately half of the sulphur is converted into the trioxide. At still higher pressures the quantity of sulphur trioxide formed is less than this, and at atmospheric pressure the gas resulting from the combustion of sulphur contains 2 per cent of sulphur trioxide and 98 per cent of sulphur dioxide.

According to Hempel, in order to determine the several amounts of these two substances in the gases resulting from the combustion of sulphur, the outlet tube of the autoclave was opened and the sulphur dioxide absorbed by drawing the gases through an absorption flask containing iodine solution. In order to effect the most complete separation of the sulphur dioxide from the trioxide, the autoclave was placed in hot water. The sulphur dioxide produced was determined by titration of the iodine solution and the sulphuric acid remaining in the autoclave was determined gravimetrically. According to this author, an exact agreement of the results could not be obtained.

Theoretically, at least, it would seem possible to determine the quantities of sulphur dioxide and trioxide in a mixture of gas by determining (1) the quantity of sulphur dioxide by means of decinormal iodine, and (2) the sulphur trioxide by a gravimetric determination of the total sulphur in the solution after absorption. In order, however, that these methods may be employed to advantage in the actual study of sulphur-dioxide disinfection it is essential that they be rapid and easy of execution. The attempt was made therefore to determine both the sulphur dioxide and trioxide volumetrically. This we have been able to accomplish in two ways:—(1) By passing the gases resulting from the combustion of the sulphur through a solution of decinormal iodine. In such a solution the sulphur dioxide is absorbed by conversion into sulphuric acid and any sulphur trioxide present in the gas is absorbed by the water which is present. In our earlier work on this subject the iodine solution contained in the several absorption flasks was poured into a measuring flask of convenient volume and made up to the mark with water. In an aliquot part of this solution the excess of iodine was determined by means of decinormal thiosulphate, and in another aliquot part of the solution the excess of the iodine was removed by means of a freshly prepared solution of sulphur dioxide of known strength and the total acidity of the resulting solution determined by means of decinormal sodium hydroxide, with phenolphthalein as the indicator. This method depends upon the reaction represented by the chemical equation $I_2+SO_2+2H_2O=2HI+H_2SO_4$, and hence for every equivalent of iodine used up theoretically 2 equivalents of acid should result, or, if 10 cc. of a decinormal solution of iodine be used up in this process, 20 cc. of decinormal sodium hydroxide should be required to neutralise the resulting solution exactly. If now a larger quantity than 20 cc. of decinormal sodium hydroxide be required, the excess is a measure of the sulphur trioxide resulting from the combustion of the sulphur, provided the solution of sulphur dioxide employed in the removal of the excess of iodine does not contain any sulphuric acid. By this method we were able to measure the quantity of sulphur trioxide formed in the burning of sulphur and to prove to our satisfaction that a certain amount of this substance did result in the combustion of sulphur. (That small quantities of sulphur trioxide are formed during the combustion of sulphur is evident from the fact that during the combustion, oily drops of sulphuric acid make their appearance on the walls of the tube.) This method has the disadvantage, however, that the solution of sulphur dioxide has to be prepared fresh every day, and the strength of the solution was found to be very subject to change and hence had to be determined practically for each determination. Fortunately, for the purpose of this investigation it was found that both of these gases could be determined (2) by means of a decinormal iodine solution, decinormal thiosulphate, and decinormal sodium hydroxide without resorting to the solution of sulphur dioxide. The method finally employed in our determinations is as follows:—

The gases resulting from the combustion of the sulphur are absorbed in a known volume of decinormal iodine solution. The liquid is then poured into a measuring flask of convenient volume and made up to the mark with water. In an aliquot part of this solution the excess of iodine is determined by means of a decinormal thiosulphate, and in this same portion the acid is determined by means of decinormal sodium hydroxide, phenolphthalein being the indicator. The quantity of iodine originally employed minus the quantity remaining unchanged as indicated by the thiosulphate gives the quantity of sulphur dioxide, and

Results of Experiments on the Combustion of 0·1 grm. of Sulphur in Air and Oxygen under the Conditions indicated in the Table.

No. of experiment.	Conditions.	Found. Sulphur burned to SO_2.	Found. Sulphur burned to SO_3.	Found. Total.	Per cent of sulphur burned to SO_2.	Per cent of sulphur burned to SO_3.	Total per cent of sulphur found.
1.	In air	0·09426	0·006884	0·101144	94·26	6·88	101·14
2.		0·09288	0·007614	0·100494	92·88	7·61	100·49
3.		0·09183	0·007690	0·09952	91·83	7·69	99·52
	Average, Series I.	0·09299	0·007396	0·100386	92·99	7·39	100·38
4.	In moist air	0·09153	0·00787	0·0994	91·53	7·87	99·40
5.		0·09578	0·00413	0·0999 (*a*)	95·78	4·13	99·91
6.		0·09153	0·00787	0·0994	91·53	7·87	99·40
	Average, Series II.	0·09294	0·00662	0·09956	92·94	6·62	99·57
7.	In air dried over sulphuric acid and lime	0·09049	0·009510	0·1000	90·49	9·51	100·00
8.		0·09373	0·006700	0·10043	93·73	6·70	100·43
9.		0·09316	0·006020	0·09918	93·16	6·02	99·18
10.		0·09456	0·005214	0·099774	94·56	5·21	99·77
	Average, Series III.	0·09298	0·006888	0·099868	92·98	6·88	99·87
11.	In dry air containing large quantity of carbon dioxide	0·09309	0·00657	0·09966	93·09	6·57	99·66
12.	In dry oxygen	0·09600	0·00314	0·09914	96·00	3·14	99·14
13.		0·09704	0·00240	0·09944	97·04	2·40	99·44
14.		0·09790	0·00270	0·1006	97·90	2·70	100·60
15.		0·09608	0·00347	0·09955	96·08	3·47	99·55
16.		0·09665	0·00257	0·09922	96·65	2·57	99·22
17.		0·09698	0·00230	0·09928	96·98	2·30	99·28
	Average, Series IV.	0·09677	0·00276	0·09953	96·77	2·76	99·53
18.	In moist oxygen	0·09893	0·00250	0·10143	98·93	2·50	101·43
19.		0·09776	0·00269	0·10045	97·76	2·69	100·45
20.		0·09720	0·00278	0·09998	97·20	2·78	99·98
	Average, Series V.	0·09796	0·00266	0·10062	97·96	2·66	100·62
21.	In a mixture of oxygen and carbon dioxide	0·09488			94·88		
22.		0·09763			97·63		
23.		0·09577			95·57		
24.		0·09689			96·89		
25.		0·09778			97·78		
26.		0·09743			97·43		
	Average, Series VI.	0·09673	0·00327 (*a*)	0·1000	96·73	3·27 (*a*)	100·00 (*a*)
27.	In equal parts by volume of oxygen and nitrogen	0·09552	0·0057	0·10122	95·52	5·70	101·22
28.		0·09233	0·0077	0·10003	92·33	7·70	100·03
	Average, Series VII.	0·09392	0·0067	0·10062	93·92	6·70	100·62
29.	In a mixture of 3 parts of oxygen and 1 part of nitrogen	0·09694	0·0029	0·09984	96·94	2·90	99·84
30.		0·09901	0·0023	0·10131	99·01	2·30	101·31
	Average, Series VIII.	0·09797	0·0026	0·10057	97·97	2·60	100·57

(*a*) By difference.

the excess of acidity over and above the amount which should result from the action of the iodine on the sulphur dioxide gives the sulphur trioxide resulting from the burning of the sulphur. Obviously, this method is based on well-known reactions employed in iodometry and acidimetry, and depends finally on the fact that the substances resulting from the action of iodine on sodium thiosulphate are neutral to phenolphthalein. The exact strength of the thiosulphate solution used was determined by means of Kahlbaum's re-sublimed iodine immediately before each experiment, and the exact strength of the iodine solution determined by means of the thiosulphate. The exact strength of the sodium hydroxide was frequently determined by titrating against weighed amounts of pure oxalic acid. The strict observance of these precautions is necessary if concordant results are to be obtained by this method. A specimen of crystallised sulphur was selected for the investigation. This was twice distilled and each of the first portions of the distillate were rejected. The product thus obtained was broken up into small pieces about the size of bird shot and preserved in a weighing bottle. In all our determinations 0·1 grm. of this was weighed out in a porcelain boat, which was then placed in a piece of Jena glass combustion tubing, 30 inches in length. One end of this long tube was drawn down to a tube of smaller calibre and connected with a train of five Drexel absorption bottles, the first four of which contained known amounts of tenth-normal iodine solution, and the last one from the tube contained a 2 per cent solution of potassium iodide. The last absorption bottle was connected with an aspirator bottle. The porcelain boat containing the sulphur was placed about four inches from the farther end of the tube away from the absorption bottles, and this end of the tube was then closed with a cork through which passed a piece of glass tubing about three-sixteenths inch in diameter, one end of which was drawn down so as to give an

opening about one-sixteenth of an inch in diameter into the larger tube. Through the smaller tube the air or oxygen required in the combustion of the sulphur was drawn by the aspirator bottle at the end of the train of absorption flasks. Care was taken so to regulate the combustion of the sulphur as to insure complete combustion and no volatilisation to the colder parts of the tube. The tube was of such length as to insure complete combustion of the sulphur long before any small amounts that might be volatilised could reach the absorption bottles. In a few of our experiments the sulphur to be burned was spread along the combustion tube over a considerable length, but always from the absorption bottles.

After the combustion was complete, the contents of the tube and bottles were transferred to a measuring flask and made up to the mark with the washings from the tube and absorption bottles. An aliquot portion was then titrated with sodium thiosulphate. From the number of cc. of iodine used up, the weight of the sulphur burned to sulphur dioxide was calculated. After adding a few drops of phenolphthalein, the acidity of the solution was determined by means of N/10 sodium hydroxide. The number of cc. of caustic soda required was recorded as "found acidity." From the quantity of iodine entering into reaction with the sulphur dioxide, the acidity resulting from the conversion of sulphur dioxide into sulphuric acid by means of iodine can be calculated. The found acidity minus the calculated acidity gives the acidity due to sulphur trioxide. From this the weight of the sulphur burned to sulphur trioxide may be calculated, and this, added to the weight of the sulphur burned to sulphur dioxide, gives the total weight of the sulphur burned. The results of our determinations are given in the accompanying table.

It will be seen from an examination of the results given in the table—

1. That there is a reasonable agreement between our determinations and those of Hempel, of the several amounts of sulphur dioxide and sulphur trioxide which result from the burning of sulphur in oxygen, especially when the fact that the combustion was carried out in a somewhat different manner in the two cases is kept in mind. According to Hempel, 2 per cent of the sulphur is burned to sulphur trioxide; according to our determinations, Series IV., 2·76 per cent of sulphur is burned to the trioxide.

2. It is further evident from our results that considerably larger amounts of sulphur trioxide are formed when sulphur is burned in air than when it is burned in oxygen. That such is the case may be seen from the results given in Series I., II., III., IV., and V. From an average of all of our results bearing on this point, it will be seen that about 2·5 times as much sulphur is burned to sulphur trioxide in air as is burned to sulphur trioxide in oxygen.

3. The results obtained in Series I., II., III., and in the single experiment No. 11 would seem to indicate that moisture, dryness, and the presence of increased amounts of carbon dioxide are practically without influence on the combustion of sulphur in air, and from Series IV. and V. it would seem that moisture is practically without influence on the combustion of sulphur in oxygen, and from Series VI. that carbon dioxide exerts but little influence on the combustion of sulphur in oxygen, the amount of sulphur trioxide being only slightly increased over the amount of this substance formed in dry and moist oxygen.

Finally, it would seem from the results of our experiments given in Series VII. that the increased production of sulphur trioxide in air as compared with oxygen is due in some way to the presence of nitrogen. It will be seen further from Series VIII. that a great diminution in the quantity of nitrogen as compared with the quantity present in the experiments of Series VII. and the quantity normally present in air causes a marked falling off in the production of sulphur trioxide.

It would seem therefore from our results that in the combustion of sulphur, nitrogen acts as a carrier of oxygen.

In support of this conclusion the fact may be mentioned that in the combustion of certain substances in air small amounts of nitrogen are also oxidised. For example, Kämmerer (*Ber.*, x., 1684) proved the presence of nitrogen peroxide in the gases left after burning magnesium in air, by the characteristic odour and colour of the gas and by the formation of the iodide of starch on the addition of the potassium-iodide-starch reagent. Dixon and Russell have also observed that when an explosive mixture of carbon bisulphide and oxygen, containing small amounts of nitrogen, is ignited, some of the nitrogen is invariably oxidised (*Trans. Chem. Soc.*, 1899, pp. 75-610).

The formation of small amounts of one of the higher oxides of nitrogen during the burning of sulphur in air and the subsequent oxidation of sulphur dioxide thereby would afford the simplest explanation of the fact that considerably more sulphur trioxide is formed when sulphur is burned in air and in mixtures of oxygen and nitrogen than is produced when it is burned in pure oxygen or in mixtures of carbon dioxide and oxygen. — *American Chemical Journal*, xxxviii., No. 4.

THE

USE OF FELSPATHIC ROCKS AS FERTILISERS.*

By ALLERTON S. CUSHMAN,
Assistant Director, Office of Public Roads, and Collaborator, Bureau of Plant Industry.

(Concluded from p. 230).

The Effect of Fineness of Grinding.

FROM the evidence which has been submitted in the preceding pages it may be safely concluded that the potash contained in ground felspar is at least in some part available as plant food. The question whether it can be made sufficiently available under certain conditions to be an economical substitute for concentrated and soluble potash salts remains to be determined by systematic investigation. It may have been noticed in reading the account of the foregoing experiments that in only a few cases was the fineness of the felspar material described. Each investigator considered ground felspar fine material, whether it passed an 80-mesh or a 200-mesh sieve. A standard sieve containing 200 meshes to the linear inch has openings 0·0026 inch square. A sieve of 80 meshes to the linear inch has openings about 0·0007 inch square. It is never the case, however, that a material which has been ground so that it will just pass a certain sieve will consist of particles of uniform size corresponding to the size of mesh. All ground material contains a certain proportion of very fine particles, down to those which might be characterised as submicroscopic in size. The smaller the coarser particles of a given powder which has been ground in bulk the higher will be the proportion of very fine material. This is a very important point, because it is doubtless true that the amount of decomposition caused by the action of water on ground felspar is directly proportional to the active surface area presented by unit weights of the powder. To one who has not studied the matter, the rapidity with which surface area rises with fine grinding is very surprising. In a 200-mesh felspar powder, such as is supplied by the grinder for the pottery trade, the finest particles bear the same relation to the coarsest present as these latter would to fragments about 2 inches in diameter. As the surface area of a powder increases in inverse ratio to the diameter of the particles, it can be seen how quickly the availability due to active surface must increase with fineness in grain. No one would for an instant consider the possibility of fertilising land by scattering on it felspar

* From *Bulletin* No. 104, U.S. Department of Agriculture, Bureau of Plant Industry.

TABLE IV.—*Production (short tons) and Value (dollars) of Felspar*, 1901—1905.
("Mineral Resources of the United States," U.S. Geol. Survey, 1905).

Year.	Crude.		Ground.		Total.	
	Quantity.	Value.	Quantity.	Value.	Quantity.	Value.
1901	9,960	21,669	24,781	198,753	34,741	220,422
1902	21,870	55,501	23,417	194,923	45,287	250,424
1903	13,432	51,036	28,459	205,697	41,891	256,733
1904	19,413	66,714	25,775	199,612	45,188	266,326
1905	14,517	57,976	20,902	168,181	35,419	226,157

TABLE V.—*Price per Pound of Potash Unit in Felspar.*
(Cents per pound).

Potash contained in the felspar.	Cost of ground felspar per ton (2240 pounds).									
	$1.	$2.	$3.	$4.	$5.	$6.	$7.	$8.	$9.	$10.
3 per cent	0·015	0·030	0·044	0·059	0·074	0·089	0·104	0·119	0·134	0·149
4 ,,	0·011	0·022	0·033	0·044	0·055	0·067	0·078	0·089	0·100	0·111
5 ,,	0·009	0·018	0·027	0·035	0·044	0·053	0·062	0·071	0·080	0·090
6 ,,	0·007	0·015	0·022	0·030	0·037	0·045	0·052	0·059	0·067	0·074
7 ,,	0·006	0·012	0·019	0·025	0·032	0·038	0·045	0·051	0·057	0·063
8 ,,	0·005	0·011	0·017	0·022	0·028	0·032	0·039	0·045	0·050	0·056
9 ,,	0·005	0·009	0·014	0·019	0·024	0·029	0·035	0·039	0·044	0·049
10 ,,	0·004	0·009	0·013	0·018	0·022	0·027	0·031	0·035	0·040	0·045
11 ,,	0·004	0·008	0·011	0·015	0·020	0·023	0·028	0·030	0·034	0·040
12 ,,	0·004	0·007	0·011	0·015	0·018	0·022	0·026	0·029	0·033	0·037
13 ,,	0·003	0·007	0·010	0·014	0·017	0·021	0·024	0·027	0·031	0·034
14 ,,	0·003	0·006	0·010	0·013	0·016	0·019	0·022	0·026	0·029	0·032
15 ,,	0·003	0·006	0·009	0·012	0·015	0·018	0·021	0·024	0·027	0·030

fragments of an average diameter of 2 inches. Yet in grinding these fragments to an 80-mesh powder, we have not increased the active surface area as much as we should do by pushing on the grinding of an 80-mesh powder to the ultimate fineness attainable in mechanical processes. Grinding is making surface, and it can be shown that the availability of potash in ground felspar increases with the surface area. If felspar is ground so that it will pass an 80-mesh sieve, it will of course contain a certain proportion of very fine particles, some of which approach the limits of visibility under a powerful microscope. If we carry on the grinding of the material from 80-mesh to 200-mesh, the proportion of the very small particles is enormously increased. The smallest particles which we need to consider here are those which can be measured by a micrometer device connected with the microscope. These smallest particles have a diameter of about 0·0001 mm. Now, in order to make a specific example, we will consider the surface areas presented by 1 pound of felspar in different degrees of subdivision. First, in the form of a solid cube, then broken down to particles that could just pass an 80 and a 200 mesh sieve, respectively, and, finally, in the condition it would be if it were possible to grind all the material as fine as the finest particles which occur in an ordinary 200-mesh powder. The 1 pound of felspar in a solid cube would have a surface area of 29·3 square inches; particles capable of passing an 80-mesh sieve would give 8870 square inches; particles able to pass a 200-mesh sieve would give 24,905 square inches; and if it were possible to reduce the powder to particles 0·0001 mm. in diameter, there would result a surface area of 16,460,000 square inches.

If it were practically possible to collect 1 ton of felspar all in the state of the finest particles, as shown above, the surface area presented by the ton would be enormous—in fact, it would be equal to 256,000,000 square feet, 5877 acres, or more than 9 square miles. Now, although such grinding is out of the question at the present time, an ordinary 200-mesh felspar prepared for the pottery trade, which is valued at about 8 dols. per ton, contains a large proportion of very fine particles. The marvellous rise in the surface area attained by fine grinding is very well exhibited in the figures given, and it is undoubtedly true that previous experimenters have not paid sufficient attention to the percentage of very fine material in the ground felspar.

One opponent of the use of felspar has written ("The Potash in Crushed Rock," German Kali Works, New York):—

"What we call soil is rock of various sorts crushed or broken up by weather and other agencies. The crushed granite could hardly be more fertile than a good soil. When we think that an acre of soil 1 foot deep weighs over 3,500,000 pounds, we see what a drop in the bucket a few tons of ground rock really amounts to."

As a matter of fact, discussion of the value of a few tons of fine-ground potash-bearing rock, with its millions of square feet of surface area, can not be so easily brushed aside. It is true that the soil contains many fine particles; but those which, like felspar, suffer decomposition under the action of water have presumably been already decomposed, and this new material is to replace that which has been used up or removed. Each tiny particle of felspar provides only a small increment of potash, but in a ton of fine-ground material there are many billions of particles.

Cost of Ground Felspar.

Nearly all of the felspar which is at present ground to fine powders is prepared, as has been stated, for the pottery trade. For this purpose it is necessary to use mills with specially adapted linings so that the finished product shall not become contaminated from the contact with iron or steel. The production and cost of felspar, mainly for the use of the potteries, during five consecutive years, is shown in Table IV.

For fertiliser purposes the fine grinding of felspar could be done in iron mills similar to those which are used for grinding limestone in the cement industry. The only important points to consider would be the percentage of total potash present and the fineness of grinding. At the present time there are few data available on the cost of grinding felspar to a 200-mesh powder, but with modern machinery there is little doubt that it can be done much

more economically than would have been considered possible only a few years ago. Under the stimulus of the cement industry a great development has been made in recent years in the methods and art of fine grinding. Table V. is of interest, as it shows at a glance what the potash in ground felspar would cost if the percentage is compared with a cost of grinding varying from 1 dol. to 10 dols. per long ton.

The prices are given in cents per pound, so that if, for instance, rock carrying 8 per cent of potash could be delivered for 9 dols. per ton, the potash contained in it would be added to the land at a cost of 5 cents per pound. At 5 dols. per ton the cost per pound would fall to 28 mills. The figures are of course only applicable provided the potash in the ground material can be proved available as a plant food.

It must be remembered that the only real measure of available potash is that which is made use of by the crop. It is not likely that all the potash added, even in the form of soluble potash salts, is actually used, and the amount that can be supplied by ground rock is still an unknown quantity.

Possible Harmful Effects of Ground Felspar.

The question is frequently asked whether there is possible danger to the land in experimenting with the use of ground felspathic rock. It is well known that in some cases, notably with tobacco, injurious effects are produced by the continued use of the soluble potash salts, particularly the sulphate and muriate. Felspar grains of various sizes are normally present in many soils; it does not, therefore, seem possible that any harmful effect could follow the application of ground rock. As has been pointed out in an earlier portion of this paper, felspar consists of the alkaline elements, soda, potash, and lime, combined with alumina and silica. After decomposition, hydrated aluminium silicate, the essential base of all clays, is left behind, the alkalis and the silica being set free in a condition in which they can be absorbed by the root action of plants. It would seem, therefore, that whatever the value of the results obtained no possible harm can follow the experimental use of ground felspar in reasonable quantities.

Extraction of Potash from Ground Rock.

The discussion of the use of ground rock as a source of potash is not complete unless it includes the extraction of potash by chemical and electrical processes. If future experiments should demonstrate that fast-growing crops are dependent on very soluble forms of potash, the question of the extraction of this element from ground felspar becomes a matter of importance.

The extraction of potash from rock has not as yet been accomplished on a commercial basis, but it has been done in the laboratory, and the method has been published in a recent bulletin (*Bull.* 28, U.S. Dept. of Agriculture, Office of Public Roads). The full details of the investigation are too technical for insertion here, but if the processes described could be carried on at a cost low enough, the potash in ground rock could be rendered sufficiently soluble for all practical purposes. Briefly, the method consists in sliming the ground felspar with water to which a small quantity of hydrofluoric acid has been added. This slime is placed inside a suitable wooden vessel and a current of electricity is passed through it. The alkali set free by the action of the acid is carried away by the electric current, while the acid appears to be used over and over again. Finally, by combining the acid and alkaline products, a material is obtained in which the potash which has been set free is soluble and available. It is hoped that further investigation will result in some method based on these principles for making the vast quantities of potash contained in felspathic rocks completely available.

Conclusion.

A careful reading of the foregoing pages will show that no claim has been made that ground felspar is an efficient substitute, under all circumstances, for potash salts. The effort has been to present all the evidence which could be collected, both for and against the use of ground felspar as a fertiliser. The question is still open, and systematic and long-continued experimentation is the only possible method of obtaining conclusive information on the subject. The evidence so far obtained appears to indicate that under certain conditions and with certain crops felspar can be made useful if it is ground sufficiently fine. On the other hand, it is highly probable that under other conditions the addition of ground felspar to the land would be a useless waste of money. At the present stage of the investigation it would be extremely unwise for anyone to attempt to use ground rock, except on an experimental scale that would not entail great financial loss.

The subject must be approached conservatively, with due regard to business economy. Sensationalism and exaggeration invariably do harm. It is extremely unlikely that ground rock will ever entirely displace the use of potash salts, for its availability must inevitably depend upon many modifying conditions, such as the nature of the soil, the amount of moisture present, the character of the other fertilisers used, and the varying root action of different crops. With tobacco the results so far obtained have been encouraging, but it is possible that this plant, which is a voracious feeder, can make use of the potash in fine-ground felspar to a greater extent than other fast-growing crops, such as potatoes and the cereals, some of which mature in practically sixty days and must therefore find their plant food in a highly available condition.

THE USE OF SODIUM CARBONATE AND ZINC OXIDE IN SULPHUR AND ARSENIC DETERMINATIONS.

By W. C. EBAUGH and C. B. SPRAGUE.

A METHOD involving the use of sodium carbonate and zinc oxide for sulphur and arsenic determinations was devised by one of us (C. B. S.) some years ago, and has given uniform satisfaction in various assay offices for so long a time that an account of it should be made public.

One part of dry sodium carbonate and four parts of zinc oxide are mixed thoroughly. In the case of sulphur determinations a weighed sample of the material to be analysed, usually one-half grm., is mixed intimately with enough of the sodium carbonate-zinc oxide reagent to afford at least twice as much sodium carbonate as would be required by the sulphur, arsenic, &c., present, placed in a small porcelain dish, covered with the reagent, and heated to redness in a muffle for fifteen or twenty minutes. A shorter period of heating is usually sufficient, but the time here specified is ample for all cases. The residue is then extracted with water, boiled, filtered, the filtrate made acid with hydrochloric acid, precipitated with barium chloride, and the barium sulphate treated as usual.

In an arsenic determination the substance is treated as above until the alkaline solution is filtered from the residue. This filtrate is acidified with acetie acid, precipitated with silver nitrate, boiled for a few minutes, and then filtered. The precipitate of silver arsenate is washed thoroughly with hot water, and then dissolved in dilute nitric acid, its silver content being determined finally by titration with ammonium or potassium sulphocyanate in the usual way. Ferric sulphate is used as an indicator In calculating the arsenic present use the proportion:—

3Ag : 1As :: wt. of silver found : wt. of arsenic present.

The method has been tried successfully with various sulphides such as galenite, pyrite, arsenopyrite, chalcopyrite, sphalerite, &c.; with sulphates like gypsum and anglesite; and with metallurgical products like matte speiss, and flue dust. In the case of analyses of heavy spar the method is

not superior to the ordinary fusion with an alkali. The fact that the decomposition with sodium carbonate and zinc oxide has been employed for control and umpire assays upon ores in commercial work for so long a period without objection, is evidence that the results obtained by the method are accurate.

It will be seen that the method for sulphur is a modification of the well-known Eschka method, and that for arsenic is an improvement upon Pearce's method. The advantages of the decomposition described are :—(1) That the mass resulting from the heating is not fused, but can be removed readily from the dish and leached with water; (2) the ease and speed with which sulphides, sulphates, arsenates, &c., are decomposed; (3) no time-consuming subsequent evaporations are necessary; and (4) the absence of a large quantity of alkaline and other salts from the solutions in which the precipitations of barium sulphate and silver arsenate are effected.—*Journal of the American Chemical Society*, xxix., No. 10.

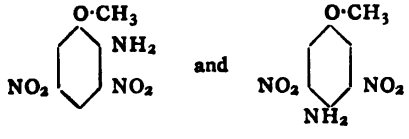
PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

THE following completes the abstracts of Papers received during the vacation, and published or passed for publication in the *Transactions* :—

178. "*The Diazotisation of Dinitroanisidines and Related Compounds.*" By RAPHAEL MELDOLA AND JAMES GORDON HAY. (*Trans.*, 1907, 1474.)

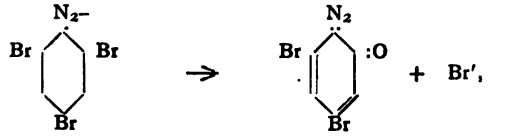
As the result of former researches, the conclusion has been reached that the configuration essential for the displacement of a nitro-group on diazotisation is that the mobile group must not only be in the ortho- or para-position with respect to the amino-group, but that there must also be another nitro-group or acid substituent in a position adjacent to the mobile group. When these conditions are not fulfilled and the methoxy-group is in the ortho- or para-position with respect to the amino-group with a nitro-group adjacent, then on diazotisation a diazo-oxide (quinonediazide) is formed with the elimination of the methyl(methoxy) group. Two instances of this type of "diazo-reaction" have been studied, and in confirmation of the general conclusions the authors have found that the two dinitro-anisidines,—



in which neither of the two sets of conditions above indicated is fulfilled, behave normally on diazotisation, losing neither nitro- nor methoxy-group. In the course of the present research, the authors have prepared 2 : 3-dinitro-4-aminophenol, the N-*acetyl* derivative of which crystallises in yellow needles melting at 199·5°. The free base is unstable, and could not be isolated. A comparative study of the products of diazotisation of this and the corresponding dinitro-*p*-anisidine has brought out very clearly the "loosening" influence of the methyl-group on the nitro-group, since under conditions in which the dinitro-anisidine loses a nitro-group on diazotisation the dinitro-aminophenol retains both nitro-groups. The 2 : 3 : 5-*trinitroaminophenol*, of which the acetyl derivative was described in a paper recently published by one of the authors (*Trans.*, 1906, lxxxix., 1935), has also been isolated, and the products of its diazotisation studied in a preliminary way.

179. "*Isomeric Change in Benzene Derivatives. Replacement of Halogen by Hydroxyl in Chlorobromodiazobenzenes.*" By KENNEDY JOSEPH PREVITÉ ORTON and WALTER WILLIAM REED. (*Trans.*, 1907, 1554).

In continuation of earlier work (Orton, *Proc. Roy. Soc.*, 1902, lxxi., 153; *Proc.*, 1902, xviii., 252; *Trans.*, 1903, lxxxvi., 796; 1905, lxxxvii., 99) on the transformations of halogendiazobenzenes, in which an atom of halogen is replaced by hydroxyl, a quinonediazide resulting, thus :—



a study has now been made of mixed symmetrical chlorobromodiazobenzenes. For this purpose, the diazo-compounds which are obtainable from 2 : 6-dichloro-4-bromo-, 2 : 4-dichloro-6-bromo, 4-chloro-2 : 6-dibromo-, and 6-chloro-2 : 4-dibromo-anilines have been used. 3-*Chloro-5-bromo-p-toluidine* (which has not been hitherto described) was also prepared for the same purpose.

From these experiments, which were carried out in the manner followed previously, two facts have been elucidated. The replacement of halogen by hydroxyl is not exclusively confined to the halogen atoms which are in the ortho-position with respect to the diazo-group. Some 20 per cent of the molecules of the diazo-compound lose an atom of halogen from the para-position, a *p*-quinonediazide being formed.

When all other conditions are alike (such as relative positions in the benzene ring, contiguity of other substituting groups, &c.), the displacement of the halogen appears to be independent of the nature of the halogen. Thus 80 per cent of the molecules of 2 : 6-dichloro-4-bromodiazobenzene and 4-chloro-2 : 6-dibromodiazobenzene respectively lose one atom of chlorine or bromine from the ortho-position; again, 50 per cent of the molecules of 3-chloro-5-bromo-*p*-diazotoluene lose an atom of chlorine from one ortho-position (with respect to the diazo-group) and 50 per cent lose bromine from the other ortho-position.

The authors consider that the position to which the hydroxyl becomes attached will depend rather on the general symmetry and configuration than on the nature of the halogen atom occupying the given position.

180. "*A New Colouring Matter from* Nyctanthes Arbortristis." By ERNEST GEORGE HILL and ANNODA PRASAD SIRKAR. (*Trans.*, 1907, 1501).

The flowers of *Nyctanthes Arbor-tristis* yield a yellow dye soluble in water. On heating the aqueous extract in dilute hydrochloric acid, a reddish brown flocculent precipitate is formed. The greater part of this is soluble in alcohol, but cannot be crystallised from this solvent. If the alcoholic solution is gently warmed with a few drops of concentrated hydrochloric acid, a bright red sediment forms, and the solution loses most of its colour. This substance crystallises from pyridine or phenylhydrazine, and has the formula $C_{20}H_{27}O_4$. It is slightly acid, very sparingly soluble in most solvents, but readily in alkalis. It forms the *acetyl* compound $C_{20}H_{26}O_3{\cdot}C_2H_3O$, but contains no methoxyl groups. It gives neither phloroglucinol nor pyrocatechol on fusion with potassium hydroxide.

The flocculent precipitate gives a bromine compound, $C_{20}H_{15}O_{18}Br_5$, which yields bromoform on warming with potassium hydroxide.

The name *nyctanthin* is suggested for the red crystalline substance $C_{20}H_{27}O_4$.

181. "*The Velocity and Mechanism of the Reaction between Iodine and Hypophosphorous Acid.*" By BERTRAM DILLON STEELE. (*Trans.*, 1907, 1641).

The velocity and mechanism of the reaction between

iodine and hypophosphorous acid have been investigated under various conditions.

It has been found that the velocity of the reaction is independent of the concentration of the iodine provided this does not fall below a certain limiting value. This behaviour is best explained by the supposed occurrence of consecutive reactions of such a nature that the iodine takes no part in the slower or controlling reaction.

The reaction is unimolecular with respect to the hypophosphorous acid, and it is catalytically accelerated by hydrogen ions, the velocity under certain conditions being directly proportional to the concentration of the latter.

Since hydrogen ions are formed during the course of the reaction, the latter becomes autocatalytically accelerated in the absence of any large initial concentration of acid.

The further oxidation of phosphorous acid to phosphoric acid by iodine is one which is retarded by the presence of hydrogen ions. It should furnish therefore an example of autocatalytic retardation.

182. "*Succinic Acid and its Potassium Salts.*" By Hugh Marshall and Alexander Thomas Cameron. (*Trans.*, 1907, 1519).

In a previous paper (*Proc. Roy. Soc. Edin.*, 1905, xxv., 401), Cameron described the preparation of crystals of acid potassium succinate showing curved faces. The authors have now continued that research, giving further particulars of these curved crystals, and, more particularly, a description of the pure potassium salts themselves, since trustworthy data concerning these have not hitherto been published. The conditions of equilibrium for aqueous solutions containing potassium and hydrogen succinates were studied at various temperatures. At the ordinary temperature, solutions having the composition of the superacid salt, $KH_3(C_4H_4O_4)_2$, first deposit succinic acid; solutions having the composition of the acid salt, $KHC_4H_4O_4$, first deposit the superacid salt. Above 30—35°, however, the acid salt is in equilibrium with a solution having a similar composition, and it would also appear that at a considerably higher temperature the same is true for the superacid salt.

It seems probable from the results obtained that the superacid salt is not merely a "molecular" compound, but that the complex ion $H_3C_4H_4O_4'$ exists in considerable proportion in the solution, especially at higher temperatures.

The acid salts, $KHC_4H_4O_4$, $KHC_4H_4O_4,2H_2O$, and $KH_3(C_4H_4O_4)_2$, were examined crystallographically; these, with the normal salt, $K_2C_4H_4O_4,2H_2O$, were the only potassium salts of succinic acid obtained within the limits of temperature covered by the investigation.

183. "*The Fluoresceins and Eosins from 4-Hydroxyphthalic, 4-Methoxyphthalic, and Hemipinic Acids.*" By Arthur Friedl, Charles Weizmann, and Max Wyler. (*Trans.*, 1907, 1584).

Resorcinol condenses readily with 4-hydroxyphthalic, 4-methoxyphthalic, and hemipinic acids, yielding the corresponding *hydroxy-*, *methoxy-*, and *dimethoxyfluoresceins*. Hydroxyfluorescein is very slightly fluorescent, whereas methoxyfluorescein, like ordinary fluorescein, is extremely so. Dimethoxyfluorescein is much less fluorescent than is methoxyfluorescein.

The corresponding tetrabromo-derivatives of these fluoresceins show corresponding differences in their fluorescent properties.

184. "*Researches on Anthraquinones and Phthaleins.*" By William Henry Bentley, Henry Dent Gardner, jun., and Charles Weizmann. (*Trans.*, 1907, 1626).

Hydroxymethylanthraquinones can be prepared in two stages from phthalic acid (or its derivatives) and the cresols (or their methyl ethers). A derivative of benzoylbenzoic acid is first prepared and subsequently condensed by sulphuric acid to the corresponding hydroxymethylanthraquinone:—

$$CO_2H\cdot C_6H_4\cdot CO\cdot C_6H_3Me\cdot OH \rightarrow \rightarrow C_6H_4\langle{}^{CO}_{CO}\rangle C_6H_2Me\cdot OH.$$

The authors have employed two condensing agents for bringing about the first reaction, namely—(1) boric acid and (2) aluminium chloride, obtaining different results in each case where this was possible. Boric acid promotes condensation in the ortho-position, whereas aluminium chloride causes condensation to take place in the para-position with respect to the hydroxyl group.

A number of condensations of phthalic and hydroxyphthalic acids with the three cresols and *m*-4-xylenol have been effected.

185. "*Derivatives of Naphthacenequinone.*" (Part II.). By William Henry Bentley, Arthur Friedl, and Charles Weizmann. (*Trans.*, 1907, 1588).

The two nitrophthalic acids condense with α-naphthol yielding nitrohydroxynaphthoylbenzoic acids, $NO_2\cdot C_6H_3(CO_2H)\cdot CO\cdot C_{10}H_6\cdot OH$, which on reduction yield the corresponding amino-acids; the latter condense in sulphuric acid to aminohydroxynaphthacenequinones, which thus contains the amino-group in the benzene ring:—

$$NH_2\cdot C_6H_3\langle{}^{CO}_{CO=}\rangle C_{10}H_5\cdot OH.$$

These derivatives dissolve in concentrated sulphuric acid with a much bluer, and in alcoholic potash with a much yellower, colour than is exhibited by 1-amino-6-hydroxynaphthacenequinone, which contains the amino-group in the naphthalene ring.

Hemipinic acid condenses with α-naphthol, yielding *hydroxydimethoxynaphthoylbenzoic acid*,—

$$(CH_3\cdot O)_2C_6H_2(CO_2H)\cdot CO\cdot C_{10}H_6\cdot OH,$$

which when heated with sulphuric acid appears to hydrolyse and also oxidise during the condensation, the product on analysis giving numbers corresponding with *trihydroxymonomethoxynaphthacenequinone*.

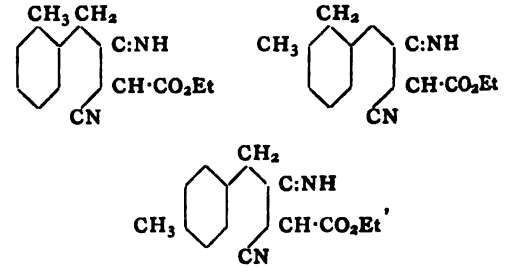
1:5-Dihydroxynaphthalene, being a di-α-naphthol, can condense with two molecules of phthalic acid, yielding *dicarboxybenzoyldihydroxynaphthalene*,—

$$CO_2H\cdot C_6H_4\cdot CO\cdot C_{10}H_4(OH)_2\cdot CO\cdot C_6H_4\cdot CO_2H.$$

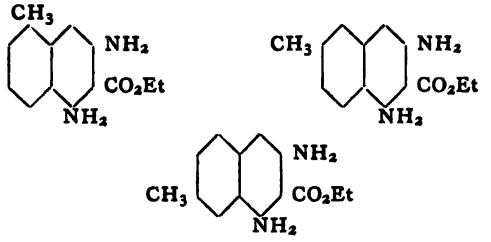
This acid, however, on condensation with sulphuric acid appears to lose one phthalic acid group, yielding a *trihydroxynaphthacenequinone*.

186. "*The Formation and Reactions of Imino-compounds.* Part V. *The Formation of Methyl Derivatives of* 1:3-*Naphthylenediamine from the Three Tolylacetonitriles.*" By Ernest Francis Joseph Atkinson and Jocelyn Field Thorpe. (*Trans.*, 1907, 1687).

In order to throw some light on the colour change which ensues when ethyl β-imino-α-cyano-γ-phenylbutyrate is transformed into the sulphate of ethyl 1:3-naphthylenediamine-2-carboxylate by the action of concentrated sulphuric acid, the three methyl derivatives of this ethyl salt, containing the methyl group in the benzene nucleus, have been prepared and investigated. These three isomeric forms of ethyl β-imino-α-cyano-γ-tolylbutyrate,—



pass on treatment with cold concentrated sulphuric acid into the corresponding methyl derivatives of ethyl 1:3-naphthylenediamine-2-carboxylate:—



These ethyl salts on hydrolysis yield the corresponding carboxylic acids, which readily evolve carbon dioxide, and pass into 1-methyl-5 : 7-naphthylenediamine, 2-methyl-5 : 7-naphthylenediamine, and 2-methyl-6 : 8-naphthylenediamine respectively.

Whereas the transformation of the meta-compound into the naphthalene ring at −5° is, like the other cases investigated previously, practically quantitative, the yield of the naphthalene derivative from the ortho- and para-compounds is scarcely 10 per cent of the theoretical, the main product of each reaction being a phenolic base which is characterised by giving an intense colour with concentrated sulphuric acid.

The malachite-green solutions which were formed at the ordinary temperature, but not at −5° in the reactions previously investigated, are therefore probably due to the formation of similar phenolic bases, since the naphthalene derivatives formed in the reactions do not themselves give colours with sulphuric acid. The following are the colour reactions of the three isomeric ethyl salts named towards concentrated sulphuric acid at the ordinary temperature.

Ethyl β-imino-α-cyano-γ-o-tolylbutyrate dissolves, forming an intense red-brown solution, which on dilution becomes first olive-green and finally yellow.

Ethyl β-imino-α-cyano-γ-m-tolylbutyrate forms a cherry-red solution, which becomes colourless on dilution.

Ethyl β-imino-α-cyano-γ-p-tolylbutyrate dissolves, forming an intense magenta-red solution, which on dilution becomes first violet, then blue, then green, and finally yellow.

No colour is formed in the case of the meta-derivative at −5°, but lowering of the temperature has no effect on the colour formation of the ortho- and para-compounds.

187. "*The Chemical Action of Radium Emanation.* Part II. *On Solutions containing Copper and Lead, and on Water.*" By ALEXANDER THOMAS CAMERON and Sir WILLIAM RAMSAY, K.C.B. (*Trans.*, 1907, 1593).

Radium emanation, as is known, yields helium when allowed to stand alone or mixed with oxygen and hydrogen gases. When dissolved in water, the gaseous product is neon, containing a trace of helium, and in presence of copper nitrate, the product is argon, containing no recognisable trace of helium. The copper solution, after the emanation has decayed in contact with it, is found to contain a trace of lithium; at the same time, the weight of the residue, which consists mainly of sodium salts, is considerably increased. The experiments were carried out in glass bulbs.

The authors suggest as a hypothesis :—(1) That helium and the α-particle are not identical; (2) that helium results from the "degradation" of the large molecule of emanation by its bombardment with α-particles; (3) that this "degradation," when the emanation is alone or mixed with oxygen and hydrogen, results in the lowest member of the series to which the emanation undoubtedly belongs, namely, helium; (4) that if particles of greater mass than hydrogen or oxygen are associated with the emanation, namely, liquid water, then the "degradation" is less complete, and neon is produced; (5) that when molecules of still greater weight and complexity are present, as is the case when the emanation is dissolved in a solution of a copper salt, the product of "degradation" of the emanation is argon. They are also inclined to believe that the copper also is involved in this process of degradation, being reduced to the lowest member of its series, namely, lithium, and they suspect that, at the same time, sodium is produced in much greater quantity than lithium. Experiments on the gases evolved from thorium nitrate show that carbon dioxide is one of the products; this might be interpreted by the same hypothesis, in supposing carbon to be formed by the degradation of thorium, the highest member of the carbon series.

188. "*Indican.*" (Part I.). By ARTHUR GEORGE PERKIN and WILLIAM POPPLEWELL BLOXAM. (*Trans.*, 1907, 1715).

Indican, $C_{14}H_{17}O_6N,3H_2O$, crystallises from a mixture of benzene and alcohol in anhydrous prisms, m. p. 176—178°, and in this form can be readily re-crystallised from absolute alcohol. On hydrolysis with dilute acids in the presence of isatin, a quantitative yield of indirubin is obtained, as predicted by Beyerinck (*Proc. K. Akad. Witensch. Amsterdam*, 1899, ii., 120), but a theoretical yield of indigotin has not as yet been produced from it by a combination of hydrolysis and oxidation. When indican is digested with boiling dilute acid in absence of air, a complex reaction occurs, a trace of indole being formed together with dextrose (compare Hazewinkel, *Proc. K. Akad. Wetensch. Amsterdam*, 1900, ii., 512) and brown, amorphous substances. The main constituent of the latter, for which the name *indoxyl-brown* is suggested, has a similar composition, and closely resembles the chief constituent of indigo-brown (*Trans.*, 1907, xci., 295), with which it is, no doubt, closely allied, but, on the other hand, it is more soluble in alcohol, and differs from it in certain minor respects. It has been found possible to isolate as much as 30 grms. of crystalline indican from 1 kilogrm. of the leaves of the *Indigofera Sumatrana*.

189. "*The Occurrence of Quercitol* (*Quercite*) *in the Leaves of* Chamaerops humilis." By HUGO MÜLLER.

This paper gives a short account of the occurrence of quercitol (quercite) in the leaves of *Chamaerops humilis*, the only species of the palm family indigenous in Europe.

These leaves in the dry state yield as much as 1·35 per cent of this substance, and, as it can be obtained from them by a very simple process, may form a suitable material for its preparation.

This quercite is the dextro-modification, and is identical with that obtained from acorns.

190. "*Cocositol* (*Cocosite*), *a Constituent of the Leaves of* Cocos nucifera *and* Cocos plumosa." By HUGO MÜLLER.

Cocosite, isomeric with inosite, is contained in the leaves of *Cocos plumosa* and *Cocos nucifera*, and also in the so-called milk of the cocoanut. In general chemical character, it resembles inosite, and shows the characteristic rhodizonic acid reaction, but differs very widely in its physical properties, such as crystalline form, melting-point, and solubility in water.

A *hexa-acetate*, a *nitrate*, and *sulphonic acids* have been obtained and examined.

Cocosite still more closely resembles the quercenin found by Delachanel and Vincent in the acorn, and also the scyllit of Staedeler and Frerichs, recently re-investigated by J. Müller. It seems highly probable that these three substances are identical.

191. "*Inositol* (*Inosite*)." By HUGO MÜLLER.

The difficulty of procuring a somewhat larger supply of material for the fuller investigation of cocosite suggested a previous study of the behaviour of the isomeric inosite, when submitted to the reactions contemplated for this purpose, as the results thus obtained would serve as a guide and indirectly effect an economy in the use of cocosite.

A considerable quantity of inosite, which had been prepared from cochineal, furnished the material for this investigation.

The behaviour of inosite hexa-acetate, when submitted to the action of a saturated solution of hydrogen bromide in glacial acetic acid in the manner described by W. H. Perkin, jun., and J. L. Simonsen, has been investigated, and also the reaction of hydrogen peroxide in conjunction with ferrous sulphate on inosite according to the methods devised by Fenton.

Monobromoinosite penta-acetate, two isomeric forms of *dibromoinosite tetra-acetate*, and also *inosite dibromohydrin* have been fully examined.

On treating the monobromo-penta-acetate with zinc-dust, it loses its bromine along with one molecule of acetic acid.

If, on the other hand, the dibromoinosite tetra-acetates are treated in the same manner, phenol and acetic acid are the only products.

The treatment of inosite by Fenton's method with hydrogen peroxide yields, with a transitory dark violet-blue coloration, besides some oxalic acid, a substance which has not yet been obtained in a definite form, but from which the barium rhodizonate and potassium-croconate have been prepared.

SOCIETY OF CHEMICAL INDUSTRY.

(London Section).

Ordinary Meeting, November 4th, 1907.

Mr. R. J. Friswell in the Chair.

"*The Determination of Indigotin in Indigo-yielding Plants.*" By Cyril Bergtheil and R. V. Briggs.

The accurate determination of indigotin in the indigo plant is of considerable importance, since a correct estimate of the efficiency of the process of indigo manufacture depends thereon. A method of precipitating indigotin from an extract of the plant in boiling water by means of ammonium persulphate, proposed by Rawson in 1904 and modified by the present authors, has been shown to give correct results by comparison with those obtained by fermentation of the extract by means of the indigo enzyme (*Journ. Soc. Chem. Ind.*, 1906, xxv., 729).

This method has been criticised by Orchardson, Wood, and Bloxam, and two alternative methods proposed, one of which, depending on the same principle, is said to give results identical with those obtained by the authors' method; whilst the other, depending on the precipitation of indirubin by the action of isatin in acid solution, indicates a considerably higher potential yield of indigotin in the plant extract used (*Journ. Soc. Chem. Ind.*, 1907, xxvi., 4). The authors' original method is now verified, and some minor modifications are recommended. It is shown that neither of the methods proposed by Orchardson, Wood, and Bloxam can be used in practice, since both lead to entirely erroneous results unless the exact indican content of the samples dealt with is previously known and the methods adjusted accordingly.

The conclusion that the isatin method may under certain circumstances indicate a higher indican content in a given extract than the persulphate method is not borne out by the authors' experiments.

"*Analysis of Indigo* (Part III.) *and of the Dried Leaves of* Indigofera arrecta *and* I. Sumatrana." By R. Gaunt, F. Thomas, and W. P. Bloxam.

A summary is first given of the results of the work on indigo carried out for the Government of India at the University of Leeds during the years 1905-1907. In the present paper the exact conditions were prescribed for the preparation of pure indigotin to serve as the standard on which the tetrasulphonate process for the estimation of indigotin is based. A reply was made to certain criticisms on the tetrasulphonate process; the defects complained of were shown to be due to want of proper precaution on the part of the operators. The methods in use for the estimation of indigotin in the leaf were described. The persulphate method was found altogether faulty, as the results obtained by it were too low. The new "isatin" method was found to give much higher results, and, moreover, the method is quantitative, as proved by its action on the glucoside indican which has recently been isolated in quantity by Messrs. A. G. Perkin and W. P. Bloxam. As a result of employing the isatin process the indigo leaf is demonstrated to be capable of yielding more indigotin than had previously been supposed. Again, the percentage of leaf present in the green plant has been under-estimated in India. It is insisted that these facts are in favour of the survival of the Indian indigo industry. To this must be added the discovery by the authors of a sample of dried leaf of *I. Sumatrana*, which was twice as rich in indigotin as any specimen of *I. Sumatrana* (the more highly valued Java or Natal plant). Finally, it was submitted that the work on the indigo ferment or enzyme had not been properly followed out, and that the present reports on the Indian manufacture are eminently unsatisfactory, for:—

(1) The colour giving value of the raw materials was seriously under-estimated, whilst (2) the indigotin value of the manufactured cake was over-estimated, and this owing to the persistent use of unsatisfactory methods of analysis in lieu of adopting the tetrasulphonate process.

FARADAY SOCIETY.

Ordinary Meeting, October 29th, 1907.

Mr. N. T. M. Wilsmore, M.Sc., in the Chair.

The Chairman announced that Sir Oliver Lodge had accepted the invitation of the Council to succeed the late Sir William Perkin as President of the Society.

A paper on "*The Electrolysis of Salt Solutions in Liquefied Sulphur Dioxide at Low Temperatures*" was communicated by Dr. Bertram D. Steele. (See p. 224).

A paper on "*The Action of Aluminium Powder on Silica and Boric Anhydride*," by Mr. F. E. Weston, B.Sc., and Mr. H. Russell Ellis, B.Sc., was read in abstract by Mr. Weston, who showed, on a small scale, some of the reductions described.

The authors have studied the action of aluminium powder upon boric anhydride and silica respectively. It is shown that in the case of boric anhydride the reducing action of the aluminium depends upon the fineness of both the aluminium and the boric anhydride, *e.g.*:—

(*a*) Mixtures in molecular proportions of the finest obtainable aluminium powder and powdered B_2O_3 which has passed through a sieve of 14,400 meshes to the square inch react at once, in the cold, when started with a fuse of Mg ribbon and BaO_2 powder.

(*b*) Mixtures in proportion of Al_2 to $2B_2O_3$ only react when heated to dull redness in a muffle furnace.

(*c*) Similar mixtures to (*a*) and (*b*), but using B_2O_3 that has only passed through a sieve of 3600 meshes to the square inch, only react when heated to 300° C. and dull redness respectively.

The products of the reaction were shown to be Al_2O_3 and mixtures of boron with aluminium borides, the latter predominating in the mixture containing molecular proportions and the former in the other mixture.

In the action of aluminium upon silica the authors used for the latter kieselguhr, precipitated silica, and fine silver sand. Here, again, the action took place more readily with the finer varieties of silica, the speed and energy of the reaction being in the order—precipitated silica, kieselguhr, silver sand.

The action took place in the cold with precipitated silica and kieselguhr on being started with a fuse of Mg and BaO_2, when the constituents in the mixture were in the ratio of $3SiO_2$ to 8Al; when the mixture contained the constituents in the ratio of $3SiO_2$ to 4Al the reaction only took place on heating the mixture to dull redness. When

sand was used the mixture had to be heated to a dull redness in each case before the action commenced, and in the mixture containing $3SiO_2$ to $4Al$ free sand and free Al were found in the product.

The products of the reaction contained in all cases Al_2O_3, silicon (as shown by the production of $SiCl_4$), and probably some silicides of Al.

Dr. R. SELIGMAN suggested that some of the heat required in these reactions was furnished by the aluminium or boron, as the case may be, burning in the air. The fireproof slags obtained in many cases were being used for making acid-resisting crucibles and for other industrial purposes.

Dr. F. M. PERKIN pointed out that the difficulty of getting a fusible slag in all cases prevented the preparation in a pure state of products like boron and silicon.

Dr. F. M. PERKIN and Mr. L. PRATT read a paper on "*The Reduction of Metallic Oxides with Calcium Hydride*," and illustrated some of the reductions.

When copper oxide is mixed with calcium hydride in proportions corresponding to $2CuO + CaH_2 = 2Cu + CaO + H_2O$, and ignited by means of a match, a vigorous reaction ensues, and volumes of steam are given off. On cooling a black mass is obtained, which on treatment disintegrates, owing to solution of calcium oxide, and metallic copper in a state of fine division is obtained. Pyrolusite, hæmatite, and tin stone all behave in a similar manner. Zinc oxide appears not to be reduced. Lead sulphide and antimony sulphide both react vigorously, and during the reaction the mixture swells up considerably, rising up out of the crucible in a cylindrical form. Very little metal is produced, the bulk of the product being a dark grey mass, which appears to be a compound of the metal with calcium and sulphur.

Borax and boric anhydride also react with calcium hydride when the mixture is strongly heated in the muffle furnace. Silica in the form of fine sand only reacts after prolonged heating, but reaction takes place more readily when kieselguhr is employed. Wolframite and rutile only react with difficulty.

Experiments were also tried with metallic calcium and wolframite. In this case a particularly vigorous reaction takes place, the tungsten being melted and being obtained on cooling as a hard regulus. The heat is so great that the calcium oxide is also melted. Rutile is also reduced by calcium; the reaction, however, is not so intense, and the titanium and calcium oxide are not fused.

The action of metallic calcium upon metallic chlorides was also studied. Manganese chloride and cadmium chloride are readily reduced. When metallic calcium and strontium chloride are mixed together in molecular proportions and ignited by heating in an iron crucible by means of the blowpipe, reaction ensues: $SrCl_2 + Ca = CaCl_2 + Sr$. Very little metal, however, is obtained, probably owing to the formation of a subchloride, ClSr—CaCl. On adding two atoms of calcium the reaction is intensely vigorous, and the metal is obtained as a fused regulus. With barium chloride the reaction is less vigorous. With the alkali metals very vigorous reactions also take place.

ROYAL SOCIETY OF NEW SOUTH WALES.

General Monthly Meeting, August 7th, 1907.

H. A. LENEHAN, F.R.A.S., Vice-President, in the Chair.

THE following papers were read:—

"*Note on Copper in Andesite from near Lautoka, Fiji.*" By H. I. JENSEN, B.Sc. (By permission of the Council of the Linnean Society of New South Wales).

This paper describes the occurrence of lumps of copper ore weighing from 1 lb. in andesitic matrix. An analysis of a specimen showed that it contained 53¼ per cent Cu, 7¾ per cent Fe, and 21½ per cent S, the metallic portion being therefore a mixture of bornite and chalcocite. A microscopic examination confirmed the presence of these two minerals. The same minerals were found to occur in many of the normal andesites of the district in smaller quantity. A quantitative estimation revealed 0·034 per cent of CuO in the normal andesite. It appears from the examination of specimens obtained, that either copper ore has segregated out in the consolidation of the lava, or else, in the period of consolidation, magnetic vapours have extracted the copper from portions of the lava, and deposited it elsewhere in the mass. The copper distinctly belongs to the andesite magma of the district, and does not constitute a mere xenogenic included product. It is interesting to note that such a differentiation has there taken place in a true volcanic rock.

"*Analysis of a Specimen of Sea-water from Coogee, New South Wales.*" By C. J. WHITE, Caird Scholar, University of Sydney.

The sample analysed was a surface water collected off Coogee, New South Wales, on October 9th, 1906. Specia attention was paid to the specific gravity determinations (for the calculation of which Buchanan's hydrometer No. 6 was used), for this gives the salinity directly, and indirectly gives very valuable indications of the various constituents present (the ratio of dissolved salts to one another being practically constant for all ocean waters). The results obtained, after combining the constituents in the generally accepted way, and omitting CO_2, were:—

NaCl	27·370	grms. per kilo.
$MgCl_2$	3·884	,,
$MgSO_4$	1·667	,,
$CaSO_4$	1·264	,,
K_2SO_4	0·887	,,
$MgBr_2$	0·072	,,
MgO (by difference)	0·048	,,
Total	35·192	

In the paper the results are also expressed in terms of 100 of halogen calculated as chlorine (*Challenger* method) and compared with the mean of 77 of Dittmar's analyses.

"*Note on the Action of Lime on the available Soil Constituents.*" By F. B. GUTHRIE, F.I.C., F.C.S., and L. COHEN.

The authors have investigated the changes that take place in the amounts of water-soluble and citric-soluble potash and phosphoric acid in limed soils in pots. Three kinds of soil were used, sand, garden loam, and clay. They find that in all cases the amount of mineral plant-food soluble in water had diminished to a considerable extent in the unlimed pots after standing for a month. The effect of liming has been to lessen this loss, but it does not appear to prevent it entirely. There is less water-soluble plant-food in the limed soils after a month than in the original soils, but more than in the untreated soils after a month. The action of lime has been either to prevent the loss of soluble plant-food that is going on or to increase it by rendering soluble fresh portions of the insoluble material of the soil. In the case of the citric-soluble ingredients, the effect of liming was much less marked. There is little or no loss of the citric-soluble plant-food in the case of the untreated soil after standing a month, and these figures are not appreciably affected by liming. In the case of the loam and clay soils, there is actually less citric-soluble phosphoric acid than in the untreated soils. In other cases the increase of citric-soluble plant-food is a very slight one. The action of lime is to largely increase the amount of nitrogen as nitrites, the nitrate-nitrogen is almost the same in the limed and the unlimed soils, except with the clay soil where the nitrates are diminished. The total nitrogen as nitrite and nitrate is increased by liming, and the action of lime would appear to be to favour the development of the nitrous organism in particular.

MISCELLANEOUS.

Royal Institution.—A Christmas course of illustrated lectures, adapted to a juvenile auditory, will be delivered at the Royal Institution by Sir David Gill, K.C.B., LL.D., D.Sc., F.R.S., on "Astronomy Old and New." The dates of the lectures are December 28 (Saturday), 31, 1907, January 2, 4, 7, and 9, 1908, at 3 o'clock.

Preparation of Aluminium Carbide. — Camille Matignon. — The large quantity of heat disengaged in the combination of aluminium with carbon, $C_3+Al_4=C_3Al_4$ +245 cals. (Berthelot) indicates that the union of the two elements would probably take place without the intervention of the electric furnace. The author proved the truth of this prediction as follows:—He made an intimate mixture of lamp-black with aluminium powder by working the two constituents up with terebenthene in the proportion of 24 parts of carbon to 70 or 140 of aluminium. Then he heated the mixture for 20 minutes in a Perrot furnace, and thus obtained a mass which had a yellowish or olive green colour. Under the microscope the crystalline carbide could be seen scattered in shining globules throughout the excess of aluminium. The latter was easily eliminated by washing either with cold hydrochloric acid or cold potash. When a specimen was decomposed with water a gaseous mixture, containing 96·36 per cent of methane and 3·36 per cent of hydrogen, was obtained. Iodine and sulphur when combining with one atom of aluminium set free a quantity of heat comparable with that disengaged with carbon. In order to make the first two elements unite with the divided metal it is only necessary to produce combination artificially at one place in the mixture, and this method is also successful with carbon, provided that an excess of aluminium is employed. The two elements also unite when they are heated in the oxyacetylene blowpipe flame. Finally, aluminium carbide can be prepared by allowing the chlorides of carbon to act upon the metal. The equation is $10Al+C_6Cl_6=2AlCl_3+2C_3Al_4$ +727·6 cals. The carbide is readily separated from the volatile aluminium chloride.—*Comptes Rendus*, cxlv., No. 17.

MEETINGS FOR THE WEEK.

WEDNESDAY, 20th.—Microscopical, 8. "François Watkins' Microscope" and "A Reply to Prof. Porter's and Mr. Everitt's Criticism upon my Paper 'On the Limits of Resolving Power for the Microscope and Telescope,'" by E. M. Nelson. "Mercury Globules as Test Objects for the Microscope," by J. W. Gordon. "Light-filters for Photomicrography," by E. Moffat.

—— Society of Arts, 8. Inaugural Address of the 154th Session, by Sir Steuart Colvin Bayley, K.C.S.I., C.I.E., Vice-President and Chairman of the Council.

FRIDAY, 22nd.—Physical, 5. "Singing Sand from New England," by S. Skinner. Exhibition of a Micromanometer, by L. Bairstow. A Diabolo Experiment, by V. Boys. Exhibition of Gyroscope illustrating Brennan's Monorailway, by H. A. Wilson.

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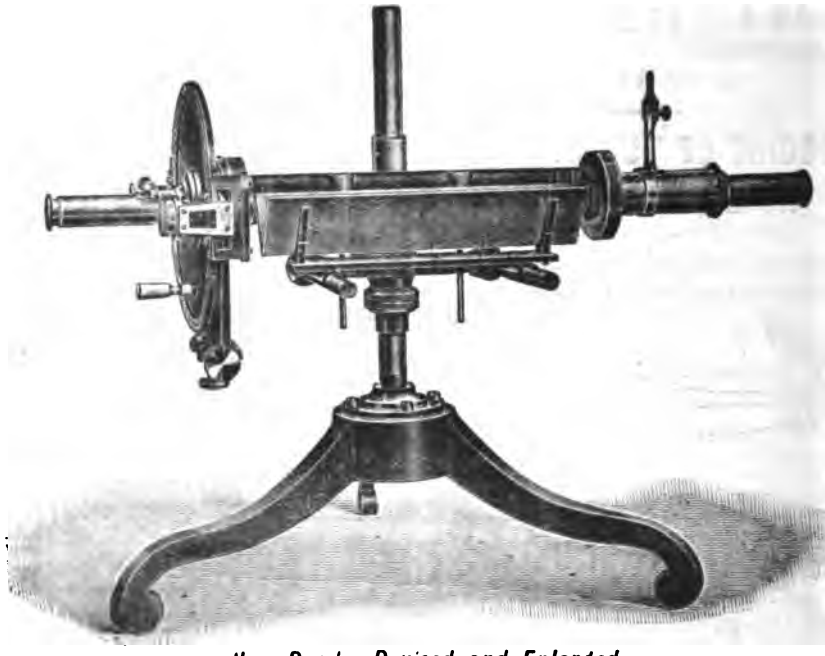

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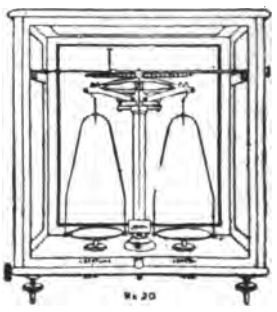

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THE CHEMICAL NEWS.

VOL. XCVI., No. 2504.

THE SO-CALLED "NERVE" OF RUBBER.

By CLAYTON BEADLE and HENRY P. STEVENS.

Now that plantation rubbers are finding their way on to the market in increasing quantities, planters and all who are financially interested in rubber plantations are carefully following the trend of prices with a view of ascertaining what reception will be given to the much larger consignments that may be expected in the course of the next year or two, and whether the present prices relative to hard-cure will be maintained. They are also anxious to discover the best method of preparation and ultimate form in which to ship their product; that is to say, whether the manufacturer will prefer to buy in the form of "block," "sheet," "crepe," "biscuit," or any other form.

We are told, and there is no doubt about it, that the methods of coagulating and curing rubber are of the greatest importance in regard to the chemical and physical properties of the crude rubber, but this is not because a certain method of coagulating and curing has some mysterious and unexplained influence on the rubber, but because the rubber is obtained more or less free from the accompanying nitrogenous and other matters, mineral and organic. The best method of coagulating and curing is that which produces a rubber with the smallest proportion of substances which are not caoutchouc, provided that powerful chemicals and extremes of temperature have not been resorted to, as these might bring about an alteration in the chemical qualities of caoutchouc.

Hence prominence has recently been given to the observations of Henri, viz., that the reticulated structure of the coagulated rubber differs according to the coagulant employed. This has been quoted as proving that the method of coagulation affects the physical properties (nerve) of the raw rubber, which is quite possible. The mere fact of a difference of reticulation can, however, have no effect whatever on the properties of the ultimate *vulcanised* product, as it is obvious that at the temperature of vulcanisation the rubber is in a semi-liquid state, and all traces of structure disappear even if such microscopic structure has not been obliterated by the previous treatment of mastication between hot rollers.

It follows from this that the physical properties and nerve of raw rubber are not so intimately connected with those of the vulcanised product as many suppose, and Henri's observation supplies evidence in this direction.

With the advent of plantation rubber the brokers have naturally applied to it those rough but practical tests which have done duty for rubber in the past, and there has consequently arisen a great deal of discussion as to whether the best plantation products really possess in the same degree as hard-cure para those varied qualities summed up by the words "nerve" or "go."

Unlike plantation rubbers, which consist of little else besides the rubber hydrocarbon or caoutchouc itself, South American and African rubbers contain varying proportions of non-caoutchouc substances, so that there is a considerable loss in the processes of washing and drying to which they are submitted by the manufacturer in Europe. These losses have been estimated and have been found to vary from, say, 15 per cent in the case of hard-cure para to as much as 50 per cent in the lowest grades, the substances removed consisting of moisture, mineral impurities, nitrogenous bodies, resins, and possibly degenerative products of the rubber itself, due to the methods of curing, or rather want of them. Many of these impurities may be detected by inspection of the raw rubbers, and other impurities make themselves apparent in a want of resilience, or "nerve," and hence the latter served as a guide in valuing a crude rubber of this class. On the other hand, it is obvious that this method must fail if used to differentiate between high-class plantation rubbers containing but traces of resinous matter and other impurities. With low grade rubbers the want of "nerve" may be taken as indicative of the proportion of resinous and similar ingredients, but to differentiate high-class plantation rubbers by means of the "nerve" is to value the caoutchouc itself by physical qualities which are dependent on the homogeneity and compactness of the sample the temperature to which it has been exposed, and many other adventitious factors. Thus it is well known that a short exposure to a comparatively low temperature is very beneficial to the physical qualities of unvulcanised rubber, as will be apparent from the figures obtained in the tests to be described in this paper.

If any doubt is cast on the value of the so-called "nerve" as a criterion, we are told that experience has shown it to be the right method of valuation, and it is the view of "practical" men generally; but what applies to wild rubbers does not necessarily apply to well prepared plantation rubbers where experience on a manufacturing scale is wanting; indeed, outside the vulcanisation tests carried out in our laboratories we are unaware of any other published work upon which an opinion could be based.

Never before have brokers or manufacturers had presented to them a raw rubber of the purity of the best plantation rubbers, and it is obvious that both methods of valuation and manufacture must necessarily be modified. In our opinion the future criterion in the valuation of a plantation rubber will be based upon purity of the raw substance and the properties of the vulcanised product. It is obvious that as practically all rubber is vulcanised in the manufacture of rubber goods, it is the properties only of the vulcanised rubber which matter, and only those properties of the raw product which indicate useful properties in the vulcanised product should be taken into consideration in valuing the raw article.

As, however, many people regard the properties of raw rubber as all important for the purposes of valuation, we shall record the results of physical tests made in our laboratories on samples of hard-cure para and plantation rubbers. The samples were tested in the same manner as described in our previous paper on vulcanising tests with plantation rubbers. In each case the figure given is the mean of at least ten determinations. The samples examined were as follows:—

1. Sample of hard-cure para taken from a freshly cut 1 af. The pieces were cut from sheets obtained by skinning off a few layers together. With a little practice such pieces can be peeled off by hand, thus yielding a sheet consisting of two or three layers firmly attached to one another.

2. Sample of hard-cure, portions of the same loaf, and obtained in the same manner as samples in No. 1, but dried in a desiccator until transparent.

3. Sample of best hard-cure para (unvulcanised) "cut sheet."

4. A quantity of hard-cure was masticated for just sufficient time to convert it into a homogeneous mass, which was then run into sheet form and the sheets tested after putting aside for a week.

5. Ceylon biscuit of the best quality procurable. The natural sheet form of the biscuit is adapted for testing without any further treatment. Of course the thickness of the sheet is not uniform, but in each case this was measured for each piece tested and the figure calculated to a sheet 1 mm. thick. The actual thickness of the biscuit tested did not exceed 1·5 mm.

6. Samples cut direct from a piece of block rubber. These samples were full of flaws and small holes as is generally the case with block, the pressure employed in compressing the sheets being insufficient to weld the whole to a compact mass free from flaws.

	Sample.	Tensile strength.		Per cent elongation		Per cent elongation after ruptured samples have been put aside for four hours.	Apparent specific gravity.
1.	Hard-cure	487		970		10·7	0·9271
2.	Hard-cure, dried	847		670		—	0·9209
3.	Hard-cure, "cut sheet"	2222		800		6·8	0·9376
4.	Hard-cure, masticated	430		300		—	0·9224
(*a*) 5.	Biscuit	468		500		2·0	0·9194
6.	Block	966		500		0	0·9060
	Block, another sample	927	929	950	672	0	0·9047
	" "	843		770		—	0·9151
	" "	981		470		—	0·9163
7.	Block	1436	1454	810	760	10·8	0·9231
	Block, another sample	1472		710			
8.	Block, masticated	518	500	300	425	—	0·9228
(*b*)	" "	483		550			
9.	Block, masticated and frozen	780		420		—	0·9214

(*a*) Mean of twenty tests.
(*b*) A small addition (1 per cent) of creosote was made during mastication of this sample.

7. Samples cut direct from a sample of very compact block almost free from flaws and air-bells.

8. A quantity of block masticated and treated exactly like the hard-cure in No. 4.

9. Sample of block pressed into sheets as in No. 8, but left in an ice chest for one week and tested two days after removal from ice chest.

(For a description of the methods of determining tensile strength and elongation, see our paper in the CHEMICAL NEWS, vol. xcvi., p. 57).

Owing to the air-bells and flaws in sample No. 6, the test pieces broke before they had time to get a really good stretching, and after rupture no elongation could be detected, although doubtless a slight elongation had taken place.

The figures under "per cent elongation at rupture" are only approximate, as it is very difficult to note the moment when the pieces begin to draw out and tear, which they do just before breaking.

The cut sheet as used in No. 3 is prepared by masticating washed and dried hard cure till perfectly homogeneous, and then compressing into a block. The block is next placed in an ice chamber and thoroughly frozen, and then cut into sheets with knives in a special machine.

A survey of the figures given in the accompanying table shows clearly the absolute futility of making tests on raw unvulcanised rubber samples unless the samples are treated in identically the same manner, both during and subsequent to the coagulation, washing, and drying. Take the case of the hard-cure para. Strips pealed off a freshly cut loaf give a tensile strength of 487, but after drying 847, and after masticating till of uniform consistency, the tensile strength falls to 430. Yet, again, if the dried and masticated rubber be exposed for a long period to a low temperature, a tensile strength of 2222 is obtained. Which of these figures is to be taken as representative of hard-cure para?

Take the case of block rubber. Six samples of block from the same plantation, prepared in the same manner, but some compressed more strongly than others, give values from 843 to 1472. Take the same block and masticate it, the figure drops to 500. What figure this block would give if frozen and treated in the same manner as the hard-cure No. 3 it is impossible to say, but the figure would probably be higher, just as block No. 8 is higher than hard-cure No. 4, masticated and treated under the same conditions. The sample of block No. 9, which had been preserved in an ice chest for one week only, showed a tensile strength of 780 as against 500 before such treatment. The Ceylon biscuit No. 5 gives low values, but then it has not been subjected to the pressure that has been employed in producing the hard-cure and block samples; the figure is only 468 in the case of the biscuit as against 1454 in the well compressed block. If the tensile strengths of the raw rubbers as found on the market were independent of the mode of preparation, and could be taken as representative of the values of these rubbers to the manufacturer, then the sample of block should fetch about three times the price of the sample of biscuit, while as a matter of fact the prices of these two particular samples were about the same, and analysis showed the same percentage of caoutchouc within 1 per cent in both.

The figures for elongation are very difficult to interpret for the same reason as in the case of tensile strength, and much the same considerations apply. The elongation at rupture is naturally somewhat low with those samples giving a low tensile strength, and the fact that biscuit No. 5 and block No. 6 showed little or no permanent elongation is probably to be explained by the fact that they broke before they had stretched to their full capacity. In the case of the block No. 6 the reason is not far to seek, as the sample was a mass of fine air-bells. The biscuit No. 5 did not show this structure on mere inspection, but on cutting a thin section and examining it under a microscope it was at once apparent that the biscuit contained a number of minute air-bells.

Perhaps the most striking proof of the influence of the conditions under which crude rubber is prepared on its physical properties may be gathered from the figures for the "apparent" specific gravity. The specific gravity of biscuit No. 5 is low, corresponding with low tensile strength. That of block No. 6 is lower still, but this is due to the greater number of large air-bells, the more compact block No. 7 giving a higher specific gravity. The hard-cure No. 2 is denser than the block. After compressing into a sheet the density of course is much increased (compare No. 8 with No. 6, from which it was prepared), but the necessity of heating the block has reduced its tensile strength; on the other hand, on freezing for one week the tensile strength has improved without materially affecting the specific gravity. The hard-cure "cut sheet" No. 3 has the highest specific gravity of any of the samples examined, which is no doubt due to the enormous pressure to which the masticated material is subjected in the course of manufacture as already explained.

Chemical Society.—Research Fund.—A meeting of the Research Fund Committee will be held in December next. Applications for Grants, to be made on forms which can be obtained from the Assistant Secretary, must be received on or before Monday, December 9th, 1907. Those Fellows who received grants in December, 1906, or whose grants allotted in December of previous years have not been closed, are reminded that reports must be in the hands of the Hon. Secretaries not later than Monday, December 2nd, next.

RESEARCHES ON THE SEPARATION OF THE EARTHS OF THE YTTRIUM GROUP.

By A. BETTENDORFF.

NOTE.—The renowned investigator of the chemistry of the rare earths, Dr. Anton Bettendorff, who died here on October 28th, 1902, left behind him a very carefully planned experimental study of the separation of the earths of the yttrium group. I have already communicated some of the results of this study to various authors (*cf.* Böhm, "Die Darstellung der Seltenen Erden," Leipzig, 1905, i., p. 480; "Abegg's Handbuch der Anorgan. Chemie," Leipzig, 1906, iii., Part I., p. 317). The complete description of the experiments in question will be all the more interesting to those chemists who are engaged in the investigation of the rare earths. Dr. Bettendorff left the work nearly ready for publication; for the purpose of reproduction here it has only had to be slightly altered and some additions made from the notes he left.—E. RIMBACH, Bonn-a-R.

Two different materials, orthite and gadolinite, were used for the following experiments on the separation of the earths of the yttrium group; these were both treated by partly different methods of separation. The results I obtained are therefore described separately in the following pages according to the materials employed.

I. ORTHITE.

The decomposition of large quantities of orthite by degrees provided me with a considerable amount of earths of the yttrium group. They had been freed from earths of the cerium group by repeated treatment with potassium sulphate, and were distinguished by a decided yellow colour, so that it seemed probable that they contained a large amount of terbium earth. Their nitrate solution gave a strong absorption spectrum of Bahr and Bunsen's erbium earth, and indications only of the bands of didymium and samarium. Their equivalent weights varied between $\overset{II}{RO}$ = 89·40 and 94·10 from orthites of different origin.

Separation by Crystallisation of the Formates.

When the earths were treated with cold dilute formic acid, care being taken to avoid heating, they dissolved to a faintly rose-red liquid, which was quite clear. After several hours the separation of a salt began, and, when accelerated by stirring with a glass rod, it was completed in twenty-four hours. The salt which separated was removed from the mother-liquor, and the latter was evaporated over lime under diminished pressure at the temperature of the room. The crystals which formed were removed separately, until the mother-liquor had a syrupy consistency and the rose-red colour had quite disappeared. The five fractions thus obtained had the following properties.

No. I. Small, almost colourless crystals. On ignition carbon separated, and they gave a dark yellow earth, the equivalent weight of which had risen to $\overset{II}{RO}$ = 103·0. The solution of the nitrate showed a decided diminution of the amount of earths giving absorption spectra. The spark spectrum of the chloride still showed the yttrium lines very faintly.

No. II. Small rose-red crystals. Yellow oxide. Nitrate solution giving strong absorption spectrum of Bahr and Bunsen's erbium earth. Spark spectrum showing yttrium lines. Equivalent weight of the oxide $\overset{II}{RO}$ = 99·0.

No. III. Small, very faintly rose-red coloured crystals, the oxide of which is light yellow. Spark spectrum of the chloride giving yttrium lines. Absorption spectrum fainter than in Fraction II. Equivalent weight $\overset{II}{RO}$ = 95·34.

No. IV. Larger, almost colourless crystals, containing a very light grey oxide. Spark spectrum of the chloride shows clearly the yttrium lines. Nitrate solution giving only a faint absorption spectrum, RO = 93·17.

No. V. Mother-liquor, colourless, syrupy, shows only a faint absorption spectrum of Bahr and Bunsen's erbium earth. The spark spectrum of the chloride gives very bright yttrium lines. Oxide almost white, equivalent weight $\overset{II}{RO}$ = 81·36.

This series of experiments shows that in the first difficulty soluble fractions of the formates of the earths of the yttrium group, an earth of higher equivalent weight can be concentrated, as M. Delafontaine stated (*Ann. Chim. Phys.*, [5], xiv., 238; *Jahresber.*, 1878, p. 255); he thought it was terbium earth. The experiments also show that the second, third, and fourth separations contain Bahr and Bunsen's erbium earth, and that the yttrium earth remains mostly in the mother-liquor.

By many systematic repetitions of the method described above with the separate fractions, finally the earths of the yttrium group of orthite were decomposed into three fractions, which possessed the equivalent weights RO = 120·0, RO = 91·70, RO = 80·50.

The Earth $\overset{II}{RO}$ = 120·0.

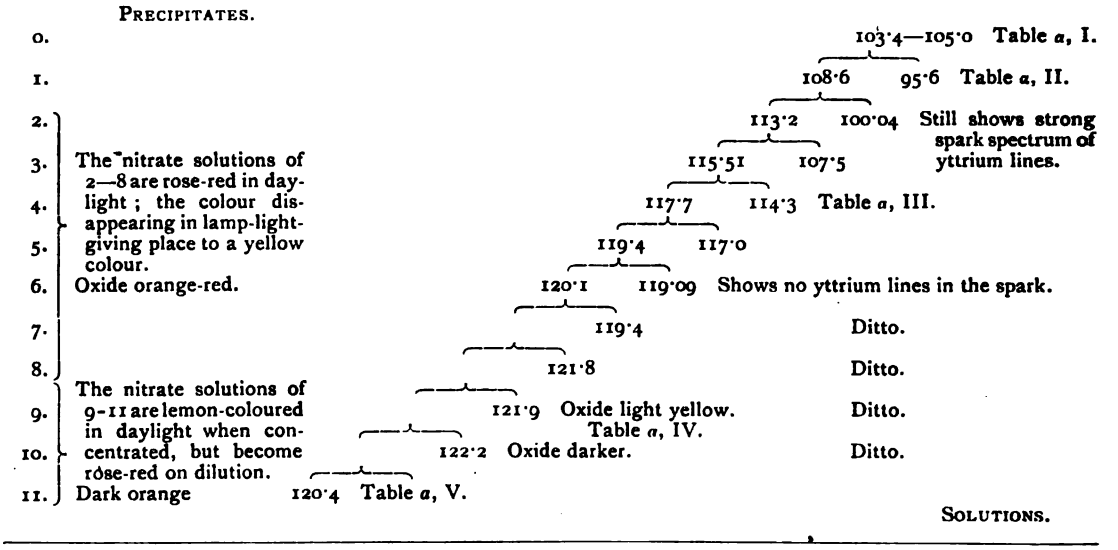
The colour of the earth RO = 120·0 was deep orange-yellow. A concentrated solution of its nitrate in a layer 0·1 m. thick gave the absorption spectrum shown in Table I., which proves that the traces of earths of the cerium group which remain in ytterite earths, even when carefully purified with potassium sulphate, especially didymium and samarium earths, are concentrated in the most difficultly soluble formates by treating with formic acid. The table further shows that the fraction $\overset{II}{RO}$ = 120·0 was quite free from Bahr and Bunsen's erbium earth.

After the nitrate of the earth $\overset{II}{RO}$ = 120·0 had been treated with potassium sulphate, to remove didymium and samarium, according to the method I have described, allowing to stand (*Liebig's Ann.*, cclvi., 160), it was shown by the subsequent partial precipitation with dilute ammonia solution that a mixture of gadolinium and terbium earths was present. It was possible to obtain, firstly, a brown oxide of equivalent weight RO = 121·57, and, secondly, a very light yellow oxide of equivalent weight 119·90 (gadolinium).

The Earth RO = 91·70.

The second fraction RO = 91·70, obtained on treating with formic acid, contained chiefly the earths giving absorption spectra and also a considerable quantity of yttrium earth, which could be detected by the spark spectrum. The oxide was still decidedly yellow, and thus probably contained terbium. As no further appreciable decomposition was effected on again treating with formic acid, the systematic partial decomposition of the nitrate was attempted in order to split it up further, and this was carried out in such a way that the greater part of the yttrium earth still contained in the oxide was removed.

The first separations, which were obtained by following the directions of Bahr and Bunsen (*Liebig's Ann.*, cxxxvii., 1), had an equivalent weight of $\overset{II}{RO}$ = 98·40 to 94·22, the ninth gave RO = 91·22, and the twentieth $\overset{II}{RO}$ = 82·0. This fraction gave a colourless solution, and the spectroscopic examination of the syrupy solution in a layer 0·1 m. thick revealed indications only of absorption bands. $\lambda = \mu\mu$ 6400, 5356, 4853, 4506 were measured. The chloride of this fraction showed a very intense yttrium spark spectrum. By putting together the nineteen fractions and further partially decomposing the nitrate, a considerable amount of oxides was again separated as the final fractions; they consisted chiefly of yttrium earths. After repeating the process four times the earths of weaker



basicity when put together had an equivalent weight of RO = 103·40 to 105·0. Their colour was light orange-yellow. As a syrupy solution of the nitrate in a layer 0·1 m. thick they showed the absorption Spectrum I. shown in Table *a*. The chloride gave a strong yttrium spark spectrum.

Separation by means of Sodium Sulphate.

It had been found that a concentrated solution of the nitrates of these oxides 103·4 to 105·0, when treated with a supersaturated solution of sodium sulphate gave precipitates of double sulphates, which dissoived in water with difficulty and contained oxides of a darker yellow colour, The nitrates obtained from these showed in the spectral apparatus a decided decrease of the earths giving absorption spectra, and their chlorides gave only a faint spark spectrum of yttrium. In the mother-liquor, on the contrary, nearly white oxides are contained; they show a very strong absorption spectrum and yttrium earth spark spectrum.

The oxides of the precipitate further differ from those of the mother-liquor very considerably in equivalent weight. Moreover, it appeared that after repeating the precipitation with sodium sulphate, the double sulphates which are insoluble in it can very soon be obtained free from yttrium earth; their equivalent weight then rises rapidly, and the colour of the oxide becomes dark orange-yellow.

The most convenient method of treating with sodium sulphate was found to be as follows:—The concentrated solution of the nitrate was as nearly as possible neutralised, and then mixed with ten to fifteen times its volume of a sodium sulphate solution saturated at 30—35° in a flask closed with a cork, and the mixture was allowed to stand for twelve hours. Then a dense precipitate of the sodium double salt separated, and above it, if the experiment was satisfactory, there was a still supersaturated solution of sodium sulphate, which contains the parts of the double sulphate easily soluble in it, namely, the yttrium and the erbium earths.

Ten grms. of the oxides are dissolved in as little as possible dilute nitric acid. The solution seldom amounts to more than 20 cc. 150 grms. of crystallised sodium sulphate are dissolved in 150 cc. of water in a stoppered flask, first putting the salt into warm water, and then mixing the two liquids when it is completely dissolved. Care is taken not to reach a temperature of 33°, because then difficultly soluble anhydrous sodium sulphate is separated. It is then tested for supersaturation by throwing in a small crystal of Glauber salt; then the Glauber salt which separates is again dissolved, so that the precipitated insoluble double salt can be separated by filtration. The earths are recovered from the filtrate in the usual way.

The difficultly soluble double sulphates thus obtained are heated with a dilute solution of oxalic acid for some time; they are thus completely converted into oxalate, and after washing, igniting, and extracting the sodium carbonate with water, they yield pure earths, the nitrate solution of which is further precipitated with a supersaturated solution of Glauber salt. The accompanying summary shows the course of the treatment of the earths of equivalent weight RO = 103·40 to 105·0, mentioned above.

Table *a* shows in Nos. II. to V. the observed changes in the absorption spectra, which were all determined in syrupy solutions, with layers 0·1 m. thick.

The experiments I have just described give the following results:—After the earths of the yttrium group have been brought to an equivalent weight RO = 91·70 (see above) by repeated treatment with formic acid, a large part of the yttrium earth being thus removed, by a series of partial decompositions of the nitrates, another considerable proportion of the yttrium earth was removed (see above) so that the equivalent weight rose to RO = 103·4 to 105·0. On treating with sodium sulphate, from the sixth precipitation onwards, yttrium-free double salts can be separated, the oxides of which have the same colour and almost exactly the same equivalent weight as the first fraction RO = 120·0 (see above) obtained by systematic repeated treatment with formic acid.

It may be said that just as yellow oxides first separate as formates, so also on treatment with sodium sulphate the first double salts which separate contain yellow oxides. In other words, both the formates and sodium sulphate double salts of the yellow oxides are difficultly soluble.

I consider that the yellow oxides obtained by the two different processes are practically identical. This opinion is confirmed by the fact that the yellow earths obtained with sodium sulphate give darker to orange-red oxides in the precipitates, while those of the solutions (see above) contain light yellow oxides.

A further confirmation of my supposition is to be found in the fact that it was possible by means of a long series of partial precipitations with dilute ammonia to decompose the yellow ytterite earths of orthite of equivalent weight RO = 120—119, obtained by treatment with sodium sulphate, into fractions of RO = 123·80—123·30, which had a brown colour, like the gold precipitated with iron vitriol, then a yellow fraction of RO = 121·30—120·80, and finally a nearly white fraction of RO = 119·7 (gadolinium).

The above-mentioned brown terbium earth precipitated with ammonia and ignited, with RO = 123·80, is a dark brown or almost black glassy material. On dissolving in nitric acid a considerable quantity of gas is evolved (O ?) while the terbium earth obtained by igniting the oxalate is lighter in colour and gives no gas when treated with nitric acid.

When gently heated in hydrogen the terbium earths turn quite white. On very strongly heating they darken more or less. When heated in a current of air the earths, which have become grey again, acquire their original orange-yellow or brown colour.

The quantity of earths of orthite giving absorption spectra, which were mentioned above, was only small. As from the method of separation they still contained yttrium earth, a closer examination of them was for the present deferred.

The Earth RO = 80·50.

It only remains to add with regard to the earth obtained as the last fraction (see above) in the separation with formic acid, that it must consist chiefly of yttrium earth. Perhaps it contains ytterbium. It is almost white, and the equivalent weight as well as the spark spectrum indicate that it contains yttrium earth. The syrupy solution of the nitrate in a layer 0·1 m. thick shows indications only of absorption bands of Bahr and Bunsen's erbium earth.

In its purification by a series of systematic precipitations in acid nitric acid solution of the oxide by H. Rowland's method, a shining white yttrium earth was separated; it possessed an equivalent weight RO = 75·17. As syrupy nitrate it showed no trace of absorption lines. On account of its properties and more especially because of the agreement of its RO with Cleve and Rowland, I consider it to be pure (see below).

II. GADOLINITE.

I had at my disposal 1 kgrm. of selected gadolinite which I had obtained from the chemical manufactory of Dr. L. C. Marquard, of Bonn. When finely powdered it was readily decomposed by sulphuric acid, and by the usual methods 434 grms. of raw earths were separated from it.

To separate the cerium group from the yttrium group the solutions of the nitrates of these earths were treated with potassium sulphate.

Two litres of a saturated potassium sulphate solution were added to 200 grms. of the earths dissolved in nitric acid, and 300 grms. of finely powdered potassium sulphate were added to the liquid in a stoppered flask. The whole was then left for several days, being repeatedly strongly shaken, until the solution above the precipitate of cerite earths-potassium double sulphates had become clear, and a thick layer of it no longer showed any didymium absorption lines. This occurred after five or six days. It was then filtered, and washed with about 1 litre of saturated potassium sulphate solution.

A layer 2 decimetres thick of the faintly red solution of the ytterite earths-potassium sulphate showed the following bands:—

Scale divisions of the apparatus.	Wave-lengths.	
14·78	6500	Er α
15·06	6388	X α
18·37	5404	These bands were observed by Krüss and Nilson in the holmium material from wöhlerite and thorite from Brevig, and were not named
18·61	5352	X γ
19·23	5222	Er β
19·39	5190	
21·25	4865	X δ
23·50	4555	X ζ

All these bands appeared comparatively very faintly.

Separation of the Double Sulphates by Crystallisation.

The faintly rose-red solution of the double sulphate was left in a large porcelain dish to evaporate at the temperature of the room, and the salt which separated removed from time to time. The first crystallisations, consisting of a mixture of rose coloured double sulphate, potassium nitrate, and potassium sulphate, gave, after dissolving in water containing nitric acid, precipitating with oxalic acid, igniting, and extracting the potassium carbonate by washing, a slightly yellow oxide with equivalent weight RO = 86·36.

The second crystallisation, which resembled it in appearance and had the same constitution, gave an oxide RO = 85·75.

The third and fourth crystallisations gave oxides of RO = 85·52 and 85·64.

The residual, very faintly coloured mother-liquor contained an oxide RO = 86·59.

These experiments show that no appreciable separation of the earths had taken place when their double sulphates were subjected to fractional crystallisation.

Separation by Auer von Welsbach's Oxide Method. (*Jahresber. d. Chem.*, 1883, 357).

When the mother-liquor, RO = 86·59, was treated by Auer v. Welsbach's oxide method, the first separation gave an oxide of RO = 93·45, the second RO = 95·65, and the third 91·12. The mother-liquor had an equivalent weight RO = 80·60. Thus by this method a decided decomposition and separation of the earths was effected, and all the above mentioned earths of the ytterite group were therefore treated in this way.

In the first series of decompositions an oxide RO = 80·60 remained behind as mother-liquor, in the second series an oxide RO = 81·80, and in the third RO = 83·24. These residues of the three series contained chiefly yttrium earth. The oxides were faintly yellow in colour, their nitrate solution was colourless, but the absorption spectrum showed that very small quantities of erbium earths were present in them. The traces of didymium oxide, which were still contained in the ytterite earths of gadolinite, in spite of careful treatment with potassium sulphate, had accumulated in the above residues. The Table β shows in II. and III. the absorption spectra of the residues of the first and third series, compared with a spectrum of didymium nitrate in I.

The equivalent weight of the fractions first separating, *i.e.*, the weaker bases, increased with the number of the series. In the eight series consecutive fractions with the following equivalent weights were obtained:—(1) RO = 104·00, (2) RO = 128·3, (3) RO = 130·54, (4) RO = 127·0, (5) RO = 126·3, (6) RO = 124·0, (7) RO = 123·8, (8) RO = 120·0, (9) RO = 115·20, (10) RO = 101·60. (Residue containing yttrium earth).

Fractions 1 to 3 must, from their preparation and equivalent weight, contain scandium and ytterbium earth. As a matter of fact, according to L. F. Nilson's statement (*Jahresber. d. Chem.*, 1880, 302), 1·2 grms. of scandium earth could be separated from the fractions by means of potassium sulphate.

The decomposition of the ytterite earths of gadolinite was proceeded with by Auer v. Welsbach's method, and it was always carried out in such a way that the greatest part of the yttrium earth, *i.e.*, the oxide of strongest basicity and smallest equivalent weight, was first removed. Then the fractions of the oxides of weaker basicity of the different series were collected by themselves. The earths giving absorption spectra then formed the middle fractions of all the ytterite earths of gadolinite.

After continuous laborious work controlled by repeated determinations of the equivalents of the fractions the following were obtained:—

1. Ytterbium material.
2. Erbium earth material (Er, Ho, Tm, Dy).
3. Yttrium earth material.

Ytterbium Earth.

There were 22 grms. of these earths obtained as the first fractions of ten series of decompositions:—

(1) RO = 126·37 (excluded), (2) 130·80, (3) 130·75, (4) 131·70, (5) 131·26, (6) 131·10, (7) 130·90, (8) 131·80, (9) 131·35, (10) 131·60 (11) 130·8.

When they were put together the concentrated solution of the nitrate, which had a distinctly reddish tinge, showed a faint absorption spectrum, which is marked No. IV. in Table β. (Twenty grms. of oxide in 100 cc.; thickness of the layer, 0·057 m.). The thulium lines appear strengthened, which agrees with the statements of Soret, Marignac, and Cleve. The oxides were free from yttrium, or at any rate no yttrium lines could be seen in the spark spectrum of the chloride.

The fractionation of the ytterbium material was effected with dilute ammonia solution in the usual way. It was now, for the first time, observed that the first and last fractions mostly had a smaller equivalent weight than the middle fractions. The first might contain scandium. In the last fractions the lowering was to be ascribed to the presence of an earth giving an absorption spectrum in which thulium bands were visible.

By removing these fractions, finally an ytterbium earth could be obtained, which, when partially precipitated with dilute ammonia, gave a series of fractions with constant equivalent weight RO = 131·0.

The ytterbium earth of equivalent weight RO = 131·0 forms a perfectly snow-white powder, and shows indications only of absorption bands in concentrated solution of the nitrate. On partial precipitation with dilute ammonia it gives gelatinous precipitates, which, when digested on the water-bath, quickly become denser, and finally crystalline. Under the microscope it is possible to detect thin hexagonal leaflets, which are completely isotropic. They are probably a basic nitrate of the earth. From the material separating in the preceding purification, which, as we saw, gave fractions of lower RO than RO = 131·0, by a fresh separation ytterbium earth of RO = 131·0 could be obtained.

In the course of the separations also an ytterbium earth of rather higher RO, *i.e.*, RO = 131·5, was obtained; it also was snow-white and had the same properties as the foregoing preparations. This was really to be expected from the composition of the original material (see above), for it contains fractions with RO = 131·80.

Which of the three ytterbium earth preparations is the purest can, in the present state of our knowledge, be decided only by spectroscopic methods. Nilson (*Comptes Rendus*, xci., 56 and 118; *Jahresber. d. Chem.*, 1880, 299) found for his ytterbium earth preparation obtained from euxenite R^{III} = 173·0. This corresponds to RO^{II} = 131·29.

Erbium Earths.

In the approximate separation of the ytterbium earths from the erbium and yttrium earths by Auer von Welsbach's method, a series of fractions was obtained, the equivalent weights of which were RO = 129·0—120·0 They gave strong absorption spectra of the erbium earths, and showed faint yttrium lines in the spark spectrum of the chlorides. To them were added the residues giving absorption spectra of the preparation of the ytterbium earths. The oxides were collected separately, and fractions were obtained with RO = 129·0—127·0, 126·5, 123·0, 120·0.

First, the fractions RO = 129·0—127·0 were decomposed into several series by systematic partial precipitation with dilute ammonia, and it was then found that a considerable quantity of ytterbium earth was still present in them. After as complete a separation as possible had been effected, the earth had an equivalent weight of RO = 126·5.

Hitherto it has always been believed that the earth which is most decidedly rose-red in colour is the one which contains the most erbium earth (Cleve, *Comptes Rendus*, xci., 381; O. Dammer, "Handb. d. Anorg. Chem.," iii., 43). I observed now that the fractions with this property are those which also possess a fairly high equivalent weight RO = 127·0—129·0, and from which, by systematic treatment, oxides of the equivalent weight of the ytterbium earth RO = 130·0—131·0 can be separated. The more the latter are removed from the fractions the more yellowish brown coloured become the earths of lower equivalent weight RO = 126·5—122·0 which remain behind. It looks to me as if the ytterbium earth obtains its beautiful rose-pink colour, which it shows when prepared from the ignited oxalate, from an oxide of lower equivalent weight and stronger basicity. In other words, it seems to me that no rose-red erbium earth exists, that the oxide which has hitherto been taken for it, and which has the equivalent weight $RO = 126{\cdot}63$, $R^{III} = 166{\cdot}0$, is only an impure ytterbium earth. We may compare with this phenomenon the blue coloration given to alumina by traces of cobalt or the green coloration given to zinc oxide by the same impurity.

In the fractions RO = 127·0—129·0 the thulium is present greatly concentrated, as may be seen from the spectral Table γ, I., and II., and it seems to me not improbable that the oxide which colours the ytterbium earth rose-red is thulium oxide.

Oxides of RO = 126·5.—The oxides of equivalent weight 126·5, which were dirty yellowish red coloured, were put together, and as they amounted to only a few grms., it was not possible to decompose them further by partial precipitation with dilute ammonia. However, I tried whether the solution of the formate gave uniform separations on fractional crystallisation by slow evaporation.

The earth RO = 126·5 dissolves in cold dilute formic acid if all heating is avoided, giving a clear rose-red solution. When evaporated over lime at the temperature of the room it gives beautiful small crystals of a decided rose-red colour which possess an oxide of RO = 126·5. The mother-liquor contains an oxide of the same equivalent weight. Thus no separation has been effected.

Oxides of RO = 120·7—123·8, 119·0—124·0. —These earths were dirty yellow coloured, and are clearly a mixture of different oxides. It almost looks as if an oxide of constant RO = 124·7 could be obtained from them. But it was impossible to continue the research in this direction also, because the quantities of the oxides were so small. A characteristic property of these earths is the fact that they are dissolved by nitric acid, giving a lemon-yellow solution, and the solution can be evaporated to a yellow syrup. If they are dissolved in a larger quantity of water, the lemon colour changes to rose-red, and on evaporation a rose coloured syrup is now obtained. If a lemon coloured nitrate solution is evaporated with sulphuric acid, lemon coloured crystals are obtained. The nitrate solution, which has become rose-red, gives, under the same conditions, rose-red salts. As regards this change of colour it is evidently the same phenomenon as is observed with the earths of orthite (see above). If the absorption spectra of the nitrate solutions of these oxides of RO = 119—124·0 are examined, both when they are yellow and red, they show no appreciable difference. However, the spectra are essentially different from those of the original material. Thus it is found that the holmium lines appear much strengthened. This is seen very clearly if we compare No. IV of Table δ with No. III. of Table γ. The oxide which belongs to the first spectral table has an equivalent weight of RO = 126·5, and the other has an equivalent weight of RO = 120·0—123·8 (119—124). The strength of the bands ascribed to erbium is the same in both tables, but the holmium bands are much stronger, and also new bands of holmium appear, which are otherwise visible only in very concentrated solutions of the original material. The well known fact that holmium earth possesses a stronger basicity than erbium earth is thus confirmed, for the earths 120·0—123·8 were obtained on partial fractionation with dilute ammonia, after the separation of the erbium earth.

If the comparison of the absorption spectra is extended

to Table *a*, Nos. IV. and V., it is found that here only holmium bands appear. This absorption spectrum is that of a nitrate solution of the dark orange-red terbium earths of equivalent weight 120·4 (see above) obtained from orthite; these earths were separated by means of a supersaturated solution of sodium sulphate, and were found to contain holmium, but to be free from erbium.

Hence we must conclude that the separation of holmium earth from erbium earth proceeds decidedly more quickly and more completely in supersaturated sodium sulphate solution than by partial precipitation with dilute ammonia.

As the terbium earth RO = 120·4, rich in holmium earth, gives a yellow solution, and thus behaves in this respect like the earths RO = 120·0—123·8, it must be supposed that holmium and its salts give yellow solutions.

Yttrium Earth from Gadolinite.

From 1 kgrm. of selected gadolinite, after the removal of the earths of the cerium group with potassium sulphate (see above) and of the weakest bases of the yttrium group by Auer von Welsbach's oxide method (see above), I obtained a liquor very rich in yttrium earth containing about 194 grms. of earth. It still contained traces of didymium and erbium earth, and the raw earth gave an equivalent weight of RO = 81·40. The liquor, the volume of which was 600 cc., was fractionally precipitated with potassium ferrocyanide in portions of 200 cc., according to Rowland's method (*Johns Hopkins Univ. Circular*, May, 1894; CHEMICAL NEWS, lxx., p. 68; also *Am. Chem. Journ.*, xvii., 154). To each 200 cc. 30 cc. of concentrated nitric acid and 500 cc. of water were added, and 50 cc. of a solution of potassium ferrocyanide, saturated at the temperature of the room, and diluted with 50 cc. of water, were added to the whole; the mixture was stirred, and allowed to stand for twelve hours. Soon a turbidity appeared, and gradually became more marked, until after the twelve hours a fine heavy reddish white precipitate had settled. As it could not be separated by filtration (it runs through the thickest filter-paper) the clear supernatant liquid was carefully drawn off. The precipitate, consisting of ferrocyanides, was decomposed by boiling with aqueous ammonia, the hydrated oxides thus obtained were filtered off, carefully washed, and ignited. Then the residue was dissolved in hydrochloric acid, and separated from the iron of the potassium ferrocyanide by means of oxalic acid. To purify further the oxide obtained from the oxalate it was dissolved in nitric acid and again precipitated with oxalic acid. When ignited and washed with water to remove all traces of alkali, the first oxide thus obtained by partial precipitation with potassium ferrocyanide was an earth of a decided yellow colour; its equivalent weight was RO = 87·0. It was found that the traces of the erbium earths of the original material were concentrated in it. A second precipitation with 10 cc. of potassium ferrocyanide solution, diluted with the same volume of water, gave a further precipitate, which, when treated in the same way, gave an earth of RO = 84·7. By systematically proceeding in this way oxides with continually decreasing equivalent weights were obtained; they became lighter as the RO diminished, and finally became white, when their ferrocyanides could readily be filtered. Finally, there remained in the solution an earth which could not be precipitated with potassium ferrocyanide, and which was separated with oxalic acid. After purification it had an equivalent weight of 76·0—76·58. This part was removed separately, while the oxides with the higher RO were again put together in order to separate again by fractionation the parts of equivalent weight RO · 76·0—76·58.

When about 25 grms. of this yttrium earth of RO · 76·0—76·58 had been prepared, and it was found that no trace of the absorption bands of erbium earth was to be observed in the syrupy solution of the nitrate, while, on the other hand, bands of didymium appeared very clearly, it was treated with potassium sulphate to remove the latter constituent. The syrupy nitrate solution. which had been neutralised as far as possible by prolonged heating on the water-bath, was diluted with much water, poured into a flask which contained saturated potassium sulphate solution and a considerable quantity of finely-powdered solid potassium sulphate. The total volume of the liquid amounted to 700 cc. After the action had been allowed to continue for two days, the mixture being occasionally strongly shaken, a small quantity of a reddish precipitate of the double sulphate of didymium was obtained. When the action and shaking were continued for a longer time, after about eight days a copious precipitate of glittering white double salt resulted. After a further action, lasting three weeks, the precipitate was separated by filtration; the filtrate of about 650 cc. I denote by the letter A. The precipitate was washed five or six times with saturated potassium sulphate solution, and the washings collected by themselves. These I shall call C and the washed precipitate *c*. The equivalent weight determinations of the purified oxides of these fractions gave for A an RO = 75·69, for C an RO = 75·7, and for *c* an RO = 76·82.

The quantity of the oxides of A and *c* amounted to 11·5 grms. They were perfectly white in colour, as syrupy nitrate gave no trace of an absorption spectrum, and their chlorides gave a brilliant yttrium spark spectrum. The quantity of oxide of C was 13 grms. It was yellowish in colour, showed clearly the absorption bands of didymium, and contained considerable quantities of yttrium, as the spark spectrum of the chloride indicated.

In another series of systematic precipitations with potassium ferrocyanide 39 grms. of yttrium earth with RO = 76·2 were obtained. It was treated as before, and the nitrate was freed from didymium by means of potassium sulphate. Exactly the same phenomena were observed, and at last an yttrium earth with RO = 75·55 and free from didymium was obtained. The part containing didymium possessed an RO = 76·9, and also contained large quantities of yttrium earth.

The following conclusion may be drawn from these experiments. By the aid of Rowland's method it is possible to get fairly quickly an yttrium earth of equivalent weight RO = 76·0. In it all traces of didymium oxide have accumulated. If an attempt is made to remove this by means of potassium sulphate, the formation and separation of didymium potassium sulphate is quickly effected. But in addition a slow formation and separation of yttrium potassium sulphate takes place, and it does not appear to be so easily soluble in potassium sulphate as has hitherto been believed. In the solution, according to the volume, a larger or smaller quantity of yttrium potassium sulphate always remains, and it contains an yttrium of lower RO than the precipitate. The higher RO of the latter cannot be explained by the presence of traces of didymium, and it is more probable that the rise in the value is due to another earth.

If, finally, an attempt is made to purify further the yttrium earth of equivalent weight RO = 75·55 by H. Rowland's method a yellowish ferrocyanide is obtained, which is easy to filter and to wash, but the earths separated from it show only small differences in equivalent weight, differences which lie almost within the limits of error in determining them by converting the oxides into anhydrous sulphate.

I sent to Prof. H. Kayser, who is occupied with the determination of the spectrum of yttrium earth, the sulphates of a small quantity of yttrium earth from gadolinite RO = 75·3 as well as from orthite with an RO = 75·17 (see above). He informed me that the preparations agree with one another in the chief lines, but that the yttrium earth from gadolinite shows another series of lines which is missing in the yttrium earth of orthite, but which can be seen clearly in a samarium earth prepared by me (*cf. Liebig's Annalen*, cclxiii., 164). As the yttrium earth in question gives no absorption spectrum, I must conclude from this statement of Prof. Kayser's that the samarium preparation mentioned above is not pure, but contains

another earth, which is also present in my yttrium earth from gadolinite. The yttrium earth RO = 75·3 from gadolinite would therefore also contain another earth.

In the continued systematic fractionation by Rowland's method with potassium ferrocyanide described above I had removed the greater part of the yttrium earth from the whole quantity of about 194 grms. of earths of RO = 81·40, and obtained :—

31·4 grms.	RO = 75·33	They were perfectly white.
27·0 „	= 75·80	
7·7 „	= 76·10	
52·6 „	= 76·2—76·8	They had a very faint tinge of yellow.
34·0 „	= 77·12	Somewhat more decided tinge of yellow than the preceding fractions.

In addition there were a few grms. of fractions with RO = 79·15—96·0; their colour became more decidedly yellow as the RO increased.

Moreover, by this treatment I obtained 40 grms. of a decidedly orange-yellow coloured oxide with an RO = 108·4, as the other end of the fractions first separated by potassium ferrocyanide. In this orange-yellow oxide the traces of earths giving absorption spectra which the original liquid still contained (see above) were much concentrated, with the exception of the didymium oxide which collected in the fractions with smaller RO. A syrupy nitrate solution of the orange-yellow oxides RO = 103·4 showed in a layer 6 mm. thick the absorption spectrum represented in Table E 1, which shows only erbium and holmium lines. The bands of didymium do not appear at all.

But these oxides were not always free from traces of yttrium earth, as may be deduced from the spark spectrum of the chlorine compound. Their orange-yellow colour points to the presence of a considerable amount of terbium earth, and in order to remove this I employed the method used to separate the terbium earth in the working up of orthite (see above), namely, separation in slightly supersaturated sodium sulphate solution. When the concentrated cold solution of the nitrate of the earth was added to the cold (at about 15°) supersaturated sodium sulphate solution, only a slight precipitate of a white salt resulted. It was filtered off after two days. The quantity of deep orange-red oxide obtained from it amounted to only 5·2 grms with RO = 116·75, the amount of earths used being 40 grms.

But the oxide which was separated from the filtrate had also a decidedly orange-yellow colour, in contrast to the earlier experiments. When 10 grms. of it were mixed with a sodium sulphate solution at 40° a copious white precipitate separated. The formation of terbium sodium sulphate thus seems to occur, not with $Na_2SO_4.10Aq.$, but either with $Na_2SO_4.7Aq.$ or the anhydrous salt, Na_2SO_4. This is confirmed by the phenomenon that the above-mentioned filtrate gave a precipitate on heating on the water-bath. Its oxide was orange-yellow, while the earth oxide of the part not precipitated, *i.e.*, that remaining in the solution, was white.

Moreover, the treatment with sodium sulphate did not produce an essential decomposition of this mixture of earths. The absorption spectra 2 and 3 of Table E show this. No. 2 is perfectly similar to No. 1 as regards the number and relative intensity of the bands, with the difference that in 2 some have become unmistakably fainter, while the bands at 538 appear broader than in the former spectrum. In No. 3 all the bands are visible, though weakened. The relative intensities of the bands have somewhat altered when compared with 1 and 2; thus the band 645·7—642 has become somewhat more strongly marked than the neighbouring band on the left, and 536·8—538 shows the same phenomenon. No other decided changes can be detected. The spectra were always determined in a layer of syrupy solution 6 mm. thick.—*Liebig's Annalen*, cccliii., 88).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Extra Meeting, October 18th, 1907.

Sir W. RAMSAY, K.C.B., F.R.S., President, in the Chair.

THIS meeting was held in the Theatre of the Royal Institution, by kind permission of the Managers.

The PRESIDENT, in opening the proceedings, said :—Professor Fischer needs no introduction to you; but I may remind you that he was asked to give the Faraday Lecture in 1895. At that time his health precluded him from coming to England, and we have now to congratulate him that his health has greatly recovered, and ourselves especially on his having come among us to-night to deliver the Faraday Lecture. I shall not, however, take up any more time, but at once ask Professor Fischer to deliver his address.

Professor FISCHER, speaking in German, then delivered the Faraday Lecture on "Synthetical Chemistry in its Relation to Biology" (see CHEMICAL NEWS, xcvi., pp. 207 *et seq*).

In presenting the Faraday Medal to Prof. Fischer at the conclusion of the lecture, the PRESIDENT said :—Before I call on Sir Henry Roscoe, I have great pleasure, Prof. Fischer, in the name of the Chemical Society in handing over to you this medal as a testimony of our great regard for you as our foreign member and of our affection for you as a man.

Sir HENRY ROSCOE—Mr. President, Ladies and Gentlemen, I have had the good fortune to hear many Faraday Lectures. I remember with pleasure the eloquence of Dumas; the charm of Wurtz, and the thought and beautiful diction of Helmholtz; but, Mr. President, I do not think that any of our Faraday Lectures has awakened greater interest than the one to which we have just listened; and this, not only because Prof. Emil Fischer is a master of his subject, and because he has laid before us work mainly accomplished by his own inventive brain and his own able hands, but also because the subject of the application of synthetical chemistry to biology which the lecturer has so ably brought before us is one which at the present moment is exceeded in interest and importance by no other branch of the science, not even—if I may be allowed, in the presence of the President, to say so—by that of radio-activity. Of the nature and character of the work which Prof. Emil Fischer has accomplished, the Fellows of the Chemical Society are good judges. When some years ago we learned that Emil Fischer had synthesised the sugars, all chemists were loud in their expressions of satisfaction and admiration. How much greater will those expressions be now when we learn what success has attended the apparently almost insoluble problem of the synthesis of the proteins.

If the one resembles the ascent of some unconquered Swiss peak, the other may be compared with the far greater feat of the attempt to reach the top of Mount Everest. But even supposing the last thousand feet of the mountain have proved to be too much for the strength of the mountaineer, yet the most important result has been achieved, for the route has been laid down and the directions given by which subsequent explorers may gain the summit. As Emil Fischer has already succeeded in this synthesis of the sugars, so he has pointed out the method by which he himself, as we all hope, or others following in his footsteps, will succeed in fully unravelling the constitution of those chemical mysteries, the proteins. By this grand work he has won for himself the admiration of us all—of all those who are interested in scientific discovery; and for bringing this subject before us in so able a manner I have the honour nnd pleasure of proposing a vote of thanks.

Sir JAMES DEWAR—Mr. President, Ladies and Gentlemen, I am exceedingly grateful to the Council for the honour which they have done me and more especially the Institution by asking me to second the admirable and eloquent vote of thanks which Sir Henry Roscoe has proposed. I assume that this has been conferred upon me as a tribute to the great man whom we have come here, Sir, to honour. For some thirty-four years, Faraday held the Chair which I have had the honour of holding, I am sorry to say, for now nearly thirty years. I cannot help thinking that the last portion of your address, in particular where you deal with the aims and method of the investigator, as well as the part that has been put so prominently before us by Sir Henry Roscoe, would have specially appealed to Faraday. Sometimes we have too great brilliancy in investigation. We have been told that the foundations of our science are being shaken, that we are living in an age in which the chemistry of the past will disappear, and that we shall have to reconstruct it on an entirely new basis. Now, Sir, I think you have conferred, by your work, the greatest honour upon the chemistry of the past. You have worked along the beaten lines of scientific investigation founded by Liebig, followed by Hofmann, Wurtz, Kekulé, and Baeyer, and have shown that, by following these ancient tracks, you can now assimilate new ground in a manner which these chemists would never have believed possible. In that way, Sir, you have consolidated the science of chemistry. However much, as Sir Henry Roscoe pointed out, we may wonder and admire radium, still we cannot but admit that the chemistry of carbon is the most extraordinary of that of all the elementary bodies, and that you, Sir, have done more than any man living to convince us of the possibility of yet further achievements in organic synthesis. What you have done would, I think, have appealed very much to Faraday, from the fact that you have worked in this magnificent, steady, undespairing, but yet successful way. There is a very admirable story of your great countryman, Luther, which represents the spirit of Faraday. Some very inquisitive person was anxious to obtain from Luther his opinion as to whether certain passages in the Scriptures were canonical or apocryphal, and Luther replied that the saints who particularly appealed to him were those of whom no marvellous stories had been recorded; who lived their lives without pretence like other people, and who did not desire to make themselves notorious. I am perfectly certain that was the mind of Faraday, and that is the mind of Emil Fischer. The man is sometimes greater than his work, and we admire you, Sir, not only for your work, but as a man. May I say that in coming here you have done a double honour to the Royal Institution. Perhaps you may be unaware of it. It has sometimes been said that the greatest discovery that Davy ever made was Faraday. You can hardly dissociate the one from the other. Now you have selected spontaneously this date for the first lecture of the season, although the Royal Institution really does not open until Christmas, and to-morrow is the centenary of the discovery of the alkali metals by Sir Humphry Davy. I do not know whether you knew this fact—but you have come here, and you have adorned both the names of Faraday and Davy by lecturing in the same room, which is practically in the same condition and at the same table where they have so often discoursed. I have to convey to you the hearty thanks of all the members of the Institution. We wish you long life to continue your great labours to adorn science, not only Germanic science, but the science of the world.

The CHAIRMAN having put the vote to the meeting, it was carried with acclamation.

Professor FISCHER, speaking in English, said—Mr. President, Ladies and Gentlemen, I owe you my sincere thanks for the kind recognition which you have been so good as to extend to my modest endeavours. I have felt exceedingly honoured in having received this invitation of the Chemical Society to come here to deliver the Faraday Lecture, and to pay homage to the great discoverer who so often on this very spot announced the results of his wonderful researches. But it affords me a keener pleasure to recall on this occasion the constant friendly intercourse which has existed during many generations between the English and the German men of science, and which has led to much happy exchange of scientific thought.

PHYSICAL SOCIETY.

Ordinary Meeting, November 8th, 1907.

Dr. C. CHREE, F.R.S., Vice-President, in the Chair.

Mr. J. M. GORDON was elected a Fellow of the Society.

Dr. FLEMING, in opening the Discussion on Mr. Campbell's paper "*On the Use of Variable Mutual Inductances*," asked the author how his method compared in accuracy with the Carey Foster method, using a commutator to add up the impulses. He had frequently measured mutual inductance by determining the self-inductances of the primary and secondary joined in series, with the windings first helping each other and then opposing each other. He asked if the author's methods were applicable when dealing with the high frequencies used in wireless telegraphy.

Mr. A. RUSSELL agreed with the author in thinking that mutual inductance was sometimes easier to calculate and easier to measure than self-inductance. The variable mutual inductance standard shown was very compact, and would be a great acquisition to a physical laboratory. In calculating self-inductance the variable current density over the cross-section of the wire sometimes brought in serious difficulties. The measurement of self-inductance in these cases might possibly be made by Mr. Campbell's method, but the limitations introduced into his formulæ by the assumption that the back E.M.F. was proportional to the rate at which the total current was changing would have to be considered.

Mr. CAMPBELL, in reply to Dr. Fleming, said the methods of measuring mutual inductance described in the paper were more convenient and direct reading than that of Carey Foster, although they were not so absolute. They were of higher accuracy than the difference-method, in which the primary and secondary were put in series and their combined self-inductance measured both with the windings helping and opposing. In reply to Dr. Fleming and Mr. Russell, the methods of measurement described were not intended, in general, for use with high frequencies of the order of those used in wave telegraphy, where resonance methods appear to be the only ones available. Mr. Campbell mentioned that the correction for the small inductance of the rheostat in method (B) could be got rid of by making the rheostat of constant inductance, this being attained by running a manganin and a copper wire side by side with a travelling contact across them, the current entering by the copper at one end and leaving by the manganin at the other.

A paper "*On a Freehand Graphic way of Determining Stream Surfaces and Equipotentials*" was read by Mr. L. F. RICHARDSON.

The paper shows that where an accuracy of 1 to 3 per cent of the range is sufficient, solutions of the equation—

$$\frac{\partial^2 V}{\partial x^2}+\frac{\partial^2 V}{\partial y^2}+\frac{\partial^2 V}{\partial z^2}=0$$

may be obtained by drawing equipotentials and sections of stream surfaces, and amending them freehand until the chequers which they form take the appropriate shape at each point of the field. The method can only be applied in certain types of symmetry, as where V is constant along each line of one or other of the following families of lines:—(i.) parallel straight lines, (ii.) circles with their centres on a common axis and their planes normal to this axis, (iii.) radii from a point, (iv.) the normals common to

the two surfaces of a thin shell of any shape, and (v.) a certain family of screw-threads. It is doubtful whether there are any other possible types. Within these five types of symmetry the freehand method far surpasses analytical methods in its adaptability to boundaries and boundary conditions of almost any shape which can be drawn on paper. It possesses the further advantage of being tolerably rapid and free from the danger of large blunders. It can no doubt be extended to deal with conductivity which depends on position, on the potential, or on the force. The author hopes that it may be of use to designers of electric machinery.

Mr. A. RUSSELL said that electricians had often to draw lines of force freehand. As a rule they had little more than their intuition to guide them, as the values of many of the variables were only known roughly and the bounding-curves were not simple geometrical figures. They would therefore welcome the paper, as it would enable them to improve their diagrams. The problem of the flow in two-dimensional space could in many cases be satisfactorily solved by experiment—for instance, by Prof. Hele Shaw's method. The author had shown, however, that the graphical method could be applied usefully to certain classes of problems in three dimensions which it would be extremely difficult to attack by any other method. The speaker had found difficulty in determining the "chequer ratio" in electrical problems where the extent of the field was unlimited.

Mr. A. CAMPBELL asked if the author's method would be applicable to a helix of finite length carrying a current.

The CHAIRMAN remarked that in the method described much depended on the eye, judgment, and patience.

The AUTHOR, in reply to Mr. Campbell, said his method would not apply to the case of a helix of infinite length.

A paper by Dr. J. MORROW, "*On the Lateral Vibration of Bars supported at Two Points with One End Overhanging*," was read by the Secretary.

When a bar, supported at one end and at some other point in its length, vibrates under its own mass only, the expression from which the frequency can be determined is of considerable complexity. When different values are assumed for the ratio of the overhanging length to the distance between the supports, the expression reduces to a customary form with a co-efficient depending on this ratio. In the paper this coefficient is given to six figures for a number of different ratios from zero to unity. The results show that Dunkerley's approximate values cannot be relied on to more than two figures, and that Chree's simple formula gives remarkable accuracy for cases in which the overhanging length is less than half the span.

NOTICES OF BOOKS.

Text-book of Organic Chemistry for Medical Students. By Dr. G. v. BUNGE. Translated with Additions by R. H. ADERS PLIMMER, D.Sc. (Lond.). London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1907.

THESE lectures give an interesting account of the outlines of organic chemistry, paying special attention to the constitution and properties of those compounds with which the medical student should be thoroughly familiar, and laying stress upon their medicinal uses or physiological importance. The text-book has been greatly appreciated by German students, and there seems little doubt but that the freshness of its style and its conciseness will procure for it as ready a welcome in England as abroad. For the benefit of English students the translator has made some additions to Professor Bunge's work, and has inserted explanatory notes, and an appendix upon the usual methods of identification and estimation of the constituents of an organic compound, its purification, &c. The book is one which deserves great commendation, and medical students will find that they have every reason to be grateful to Professor Bunge for showing them what is in his opinion the most profitable way of studying organic chemistry.

Chapters on Papermaking. Vols. III. and IV. By CLAYTON BEADLE. London: Crosby Lockwood and Son. 1907.

THE form in which these chapters on papermaking are put before the public is distinctly novel, and presents some excellent features. The author set a number of practical questions, the object of which was to assist workmen to prepare themselves for the examination on papermaking by the City and Guilds of London Institute. These questions were answered by workers of all classes, and their written answers are reproduced and criticised here, with comments upon the mistakes which have been made, and suggestions by the author as to the correct and complete solutions. Many of the answers were written by working men, and nearly all show a considerable acquaintance with the practical aspects of the subject. For those who are unable to attend lectures upon papermaking the book represents the best possible substitute. Interest is awakened and held by the informal style, and the critical powers are called into action in the comparison of the various answers from which quotations are made; no better method could probably be devised to make the reader think and reason for himself, while the fact that incorrect replies are often quoted, and the mistakes explained, should help the student to get a thorough grasp of the ins and outs of the art of papermaking. In these two volumes fairly advanced questions are propounded, and each question is so worded that it almost invariably leaves considerable scope for a display both of the knowledge and reasoning power of the worker.

Nature's Hygiene and Sanitary Chemistry. By C. T. KINGZETT, F.I.C., F.C.S. Fifth Edition. London: Baillière, Tindall, and Cox. 1907.

THE reader who wishes to add to his knowledge of infection and sanitation will find that by the time he has read through this book he has acquired in a pleasant and easy fashion a good deal of miscellaneous information of interest and practical value, without having unduly taxed his mental powers in the process. At the same time it is well to warn him that the author's views are not always those generally accepted, even upon some questions which are no longer regarded as doubtful; thus he considers the ether to be non-existent, believing that there is no evidence of its existence. However, eccentricity in matters of scientific knowledge does not perhaps weigh very much against the author's sound common sense with regard to sanitary questions, or the value of his advice upon such practical subjects as the basis of disinfection and the treatment of the sick. The book gives a very readable account of the chemical and hygienic properties of eucalyptus, pine, and camphor forests, and lays special stress upon the merits of the Sanitas preparations which the author has put upon the market. The chemistry of the eucalyptus is fully treated, and the relations of micro-organisms to infectious and contagious diseases are discussed. The author does a useful work in urging the need of the appointment of chemical officers of health, to help and supplement the work of the medical officer.

The Repulsion Theory. By ARTHUR PERCIVAL KNIGHT. Los Angeles: Parker and Stone. 1907.

THE fundamental assumption in this treatise is that there is no action at a distance, or attractive action, but that all natural phenomena are due to mutually repulsive contact-

actions of particles occupying space. The working out of the theory is based upon the kinetic theory of gases, and necessitates the assumption of the existence of a series of vortex systems. Thus the author regards the atom as a vortical unit, either non-rotative, as in the case of the elements of the zero group of the periodic system, or rotative, as in the case of the elements of Groups I. to VIII. of the system. The former atom is simple, and the latter either simple or complex; the atom may then be considered to be composed of subvortices, all of the same mass, that of the hydrogen equivalent. An attempt is made to demonstrate the unity of all forces, as different expressions of the repulsion due to impact, and of all forms of energy, but there are many weak points in the argument, which shows but little coherence and logical sequence, while some of the minor assumptions, such as that of valency, which is defined as the length of the axis of the atom measured in hydrogen equivalents, appear to be introduced merely for the sake of fitting in with the theory, and to show no connection with or dependence upon experimental facts or logical deductions therefrom.

The Commercial Possibilities of West Africa. By VISCOUNT MOUNTMORRES, F.L.S., F.R.G.S. Liverpool: The Offices of the Institute of Commercial Research in the Tropics. London: Williams and Norgate. 1907.

THIS paper has been reprinted for the Liverpool University Institute of Commercial Research in the Tropics, which is doing invaluable work in collecting and disseminating scientific information upon all subjects connected with the development of tropical countries. The paper, written by the Director of the Institute, was read at the Royal Colonial Institute, and gives an excellent account of the physiography of British West Africa; its mineral resources are enumerated, and a clear picture is given of the vastness of its forest wealth. As regards the ethnography of the country the Director speaks highly of the merits of some of the native races, and in conclusion he points out in what directions development is to be looked for in the not very far distant future.

Taschenbuch für die Anorganisch-chemische Grossindustrie. ("Pocket-book for the Inorganic Chemical Industries"). By Prof. Dr. G. LUNGE and Dr. E. BERL. Fourth Edition. Berlin: Julius Springer. 1907.

THE last edition of Lunge's Pocket-book has been issued in a much enlarged form, and now instead of being devoted exclusively to the manufacture of soda, potash, and ammonia, it includes many other important industries, among which may be mentioned those of illuminating gas, calcium carbide, acetylene, manures, cement, &c. A useful compilation of numerical tables gives practically all the physical and chemical data which the analytical chemist would be likely to require, and a clear summary is added of the Patent Laws and the laws relating to trade marks of different countries. In the special part an account is given of the analysis of the raw materials and finished products of all the more important industries, in each case a single standard method of determination being described if possible; thus the chemist will have no difficulty or trouble in choosing between a number of methods, and he may feel confident that the processes given possess every advantage over those omitted in the way of rapidity and accuracy, and have, indeed, a claim to be regarded as the standard methods.

New Method of Forming Organic Compounds of Phosphorus.—Berthaud (*Bull. Soc. Chim.*, [4], i., 146) finds that when phosphorus is heated in a sealed tube with methyl alcohol at a temperature not below 250°, for several hours, the phosphorus disappears completely. The products are phosphoretted hydrogen and phosphines as gases, and as a residue phosphoric and phosphinic acids to some extent, but principally tetramethyl-phosphonium hydrate, $(CH_3)_2POH$.

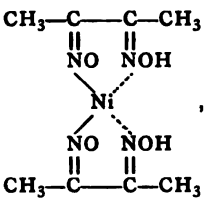
CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlv., No. 17, October 21, 1907.

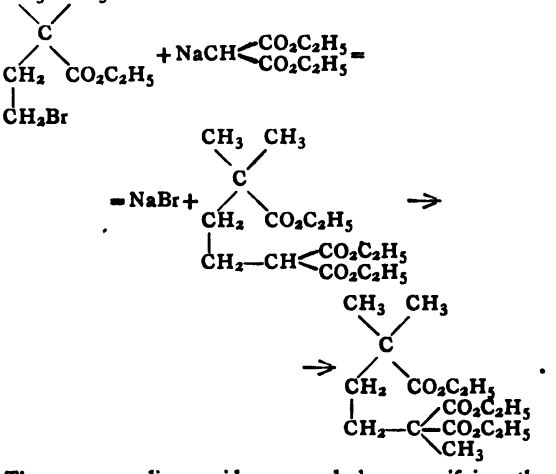
Preparation of Aluminium Carbide. — Camille Matignon.—Already noticed.

Sensitive Method of Detecting Nickel in presence of Cobalt.—Z. Tchougaeff.—Two years ago the author described (*Ber.*, xxxviii., p. 2520) the following method of detecting nickel in presence, not only of cobalt, but also of many other metals—such as magnesium, zinc, and cadmium. The method depends upon the formation of a bright red crystalline compound when dimethyl glyoxime, $CH_3—C:NOH—C:NOH—CH_3$, reacts with nickel salts in presence of ammonia. The formula of the red compound is—

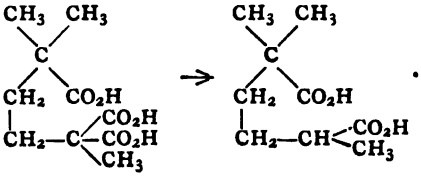


and the test is sufficiently sensitive to show the presence of 0·1 mgrm. of nickel in presence of 500 mgrms. of cobalt.

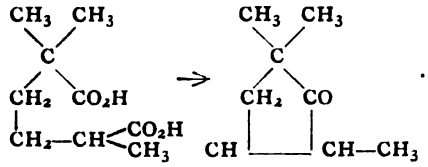
Synthesis in the Camphor Group. Synthesis of Campholene. — G. Blanc.—When 1 . 1-dimethylbutane-1 . 4 . 4-tricarboxylic ester is condensed with methyl iodide in presence of sodium ethylate campholene is formed. The 1 . 1-dimethylated ester is an oily liquid prepared by the action of sodium malonic ester upon γ-bromo- 1 . 1-dimethylbutyric ester :—



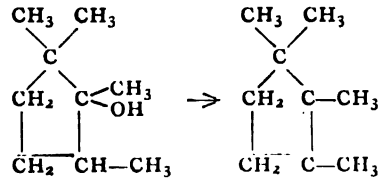
The corresponding acid, prepared by saponifying the ester with dilute potash, loses CO_2 at 205° and gives αaδ-trimethyladipic acid,—



and the latter can be converted by the action of acetic anhydride into an anhydride from which by distillation at the ordinary pressure 1 . 1 . 4-trimethylcyclopentanone-5 is obtained :—



This new ketone with methyl magnesium iodide gives a tertiary alcohol which loses water when distilled under ordinary pressure, and gives campholene :—



MISCELLANEOUS.

Society of Arts.—The programme of the arrangements for the new session of the Society of Arts has been issued, and is even fuller of interest than usual. A novel feature in it is the inclusion of a series of six lectures on Industrial Hygiene by different experts, who deal with such subjects as dust in factories and in mines, lead and mercury poisoning in pottery and match making, work in compressed air, and child labour. A course of lectures on the "Navigation of the Air" is to be given under the Shaw Trust by Dr. Hele Shaw. Four courses of Cantor Lectures are announced, the first on the Microscope, by Mr. Conrad Beck. There is a very full list of papers for the Ordinary and Sectional Meetings, and at Christmas Mr. Martin Duncan will lecture to a juvenile audience on the Cinematograph.

London Smoke: its Effect on Health.—The following is a summary of the proceedings at a Conference on this subject, held at the Institute of Hygiene, November 18th, 1907 :—

Sir William Richmond, who presided, said that experience goes to show that smoke is bad for the nervous system, bad for the bronchial tubes, bad for the eyes, and bad for the nose, but as he was not a doctor he preferred to speak of it so far as it affected himself, and its influence on works of art and decoration generally. The action of sulphuric acid present in smoke has an influence even upon marble, and will destroy copper-wire. The frescoes in the Houses of Parliament were destroyed, and much other damage could be chronicled through this cause. He quoted the late Sir William Broadbent as being a strong believer that smoke had a very bad effect on health, and he referred to the action successfully taken to save the plants at Kew Gardens, which, many of them delicate, suffer from smoke like human beings.

Dr. des Voeux said he would move the following resolution :—

> "That the coal-smoke in the atmosphere is injurious to health and lowering to vitality, and that every possible means should be adopted to find a remedy."

He described the chemical constituents of smoke, and asked what are the deleterious constituents? He said that he believed these were the sulphurous compounds. The carbon was carried into the lungs, but he did not think this did any harm—the sulphurous compounds were, however, very irritating. Dr. Ascher, a German doctor, had made a very close study of this subject, and he found that disease and mortality were greater nearer to factories and where there was much smoke, and he proved beyond a doubt that human vitality was much less when living under the influence of smoke. Smoke produced many troubles, including indigestion and catarrh of the stomach, and its worst effect was when smoke was in combination with fog. He thought the indirect effect on health was, however, even greater than its direct effects, and while he was anxious not to overstate the case he certainly thought it seriously impaired health.

Mr. Chubb dealt also with the chemical effects, and suggested the burning of smokeless fuel.

Mr. Baines said the difficulty was to find a practical remedy, and he hoped this would be proposed at the meeting.

Other speakers having stated their views the resolution was put to the meeting and carried unanimously.

MEETINGS FOR THE WEEK.

MONDAY, 25th.—Society of Arts, 8. (Cantor Lectures). "Theory of the Microscope," by Conrad Beck, F.R.M.S.

WEDNESDAY, 27th.—Society of Arts, 8. "The Franco-British Exhibition, 1908," by the Hon. Sir John A. Cockburn, K.C.M.G.

FRIDAY, 29th.—Society of Arts, 8. (Shaw Lectures on Industrial Hygiene). "The Hygiene of Work in Compressed Air (Diving, Caisson Work, Sub-aqueous Tunnelling, &c.)," by John Scott Haldane, M.A., F.R.S., &c.

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DIAMONDS.

A Lecture delivered before the British Association. at Kimberley.

By SIR WILLIAM CROOKES,
Hon. D.Sc. (Oxford, Dublin, and Cape of Good Hope), F.R.S.

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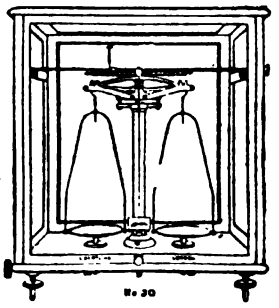

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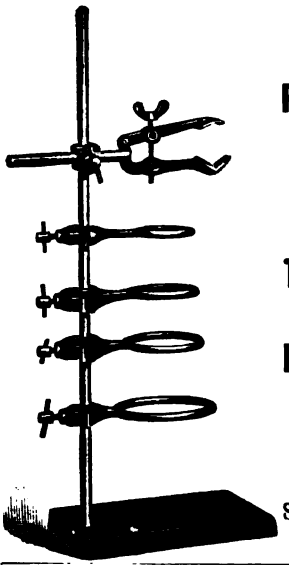

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THE CHEMICAL NEWS.

VOL. XCVI., No. 2505.

NOTE ON THE ASSOCIATION OF HELIUM AND THORIUM IN MINERALS.*

By the Hon. R. J. STRUTT, F.R.S.

THE question has been often raised of whether or not helium is a product of thorium radio-activity. My own view throughout has been that it is (*Proc. Roy. Soc.*, 1904, lxxiii., 191; also March 2, 1905). Mr. Boltwood has recently argued that the helium in radio-active minerals may always be attributed to the action of the uranium-radium series of transformations (*Am. Journ. Sci.*, February, 1907, xxiii., 77). I wish in the present note to draw attention to a case where that view is clearly untenable.

Prof. Julius Thomsen, of Copenhagen, described, in 1898 (*Zeit. Physikalische Chemie*, xxv., Part 3), a helium mineral from Ivitgut, Greenland, similar in some respects to fluor-spar, but containing rare earths. Recently he has determined the quantity of helium liberated on heating as 27 cc. per kilogrm. (*Bull. de l'Acad. Royale des Sciences, Copenhagen*, 1904, 53—57).

Prof. Thomsen kindly sent me a supply of this mineral. I have carefully tested it for radium, and find that it contains no more than the traces which are ubiquitous in rocks and minerals. The quantity found was, in fact, about the same as in average rocks, and is insufficient to account for one-hundredth part of tbe helium present.

On the other hand, a solution of the mineral gave abundant thorium emanation. I am inclined to think that there is some unknown complication about the thorium-emanating power of solutions which makes it unsafe, in certain cases at least, to infer from it the quantity of thorium present. But enough thorium emanation was given off by the solution to show that thorium was a substantial constituent of the mineral. I regard it as entirely certain that the helium in this mineral has not been generated *in situ* by uranium or radium, and have no hesitation in connecting it with the presence of thorium.

A WATER-JET BLOWER OF VERY SIMPLE CONSTRUCTION.

By S. M. REVINGTON and I. G. RANKIN.

THE blowing apparatus at present used generally consists of a copper cylinder with metal filter-pump attachment, together with gauges, &c., the cost being about 15s., and the efficiency far from excellent.

We wish to describe an apparatus we have set up for the purpose whose cost is practically nil, and which requires no skill in its manufacture.

A large bottle, say of 4 litres capacity, is fitted with a good cork pierced with holes for four tubes whose diameters are :—(A) ⅛, (B) ¼, (C) ⅜, and (D) ½ inch.

The tube A has a somewhat sudden constriction made in it. Into the upper end of this tube the jet delivers in such a way that it goes diagonally across the tube on to the side of the constricted part. We found experimentally that such a direction seems to give the best results.

It is this modification of the usual filter-pump attachment that has rendered the blower really efficient.

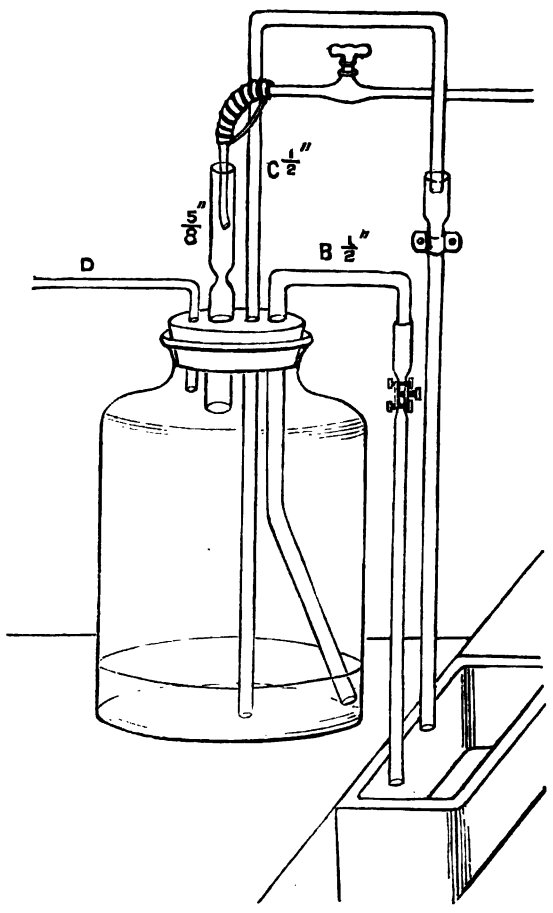
The tube B is a syphon outlet consisting of a wide bent tube passing to the bottom of the bottle and connected at the other end to similar bore tube discharging into the sink. A clip is attached to the rubber to regulate the outfall.

The tube C is a safety tube, not quite reaching the bottom of the bottle and about 2 ft. 6 in. in height, bending at the top so as to discharge into a wide tube leading to the sink.

Air passes out of the tube D, which just passes below the cork.

When the water is turned on and the air exit kept closed, as may be done by a blowpipe with air control, the pressure first starts the syphon, and afterwards air and water escape by the safety, so that the pressure quickly reaches a maximum.

On now releasing the blast, it will be found sufficient for the full gas and to work very steadily. During the course



of our present work we have joined ⅛-inch Jena tube and blown 300 cc. bulbs by its aid, and found it far superior for use with a small blowpipe to blowing with the mouth in the case of joining up long pieces of apparatus.

A platinum crucible can be kept white hot for any length of time, which is a great advantage in such cases as the ignition of $CaCO_3$ to CaO.

By blowing a tube into the side of A and connecting the jet to A with rubber tubing, the arrangement being similar to that of the head of a filter-pump, the apparatus can be employed for circulating gas when it is required to do so in large quantity.

With regard to details the position of the jet may be adjusted by noting the height of water in the safety tube, while the same holds in the case of controlling the

* A Paper read before the Royal Society, November 7, 1907.

outfall by means of the clip, care being taken that the bottle does not begin to fill. Under these conditions the amount of water used is about that taken by an ordinary Bunsen filter-pump.

It is as well also to varnish or cement the cork to preserve it and to prevent leakage of air, though the latter, if slight, is immaterial.

In conclusion, we may add that several other blowers which have since been set up in the chemical laboratories of University College have proved quite as satisfactory as our own.

MANGANESE AND THE PERIODIC LAW.

By H. REYNOLDS, B.Sc., Ph.D.

In most charts of the periodic classification of the elements the following arrangement is adopted:—

VI.	VII.	VIII.			o.	I.
S	Cl				Ar	K
Cr	Mn	Fe	Ni	Co		Cu
Se	Br				Kr	Rb
Mo	—	Ru	Rh	Pd		Ag
Te	I				Xe	Cs
	—					
W	—	Os	Ir	Pt		Au

This arrangement is based on the facts that, unless Mn were placed in the VII.th group, this group would contain only one column of elements, and that $KMnO_4$ happens to have a similar formula to $KClO_4$ and to share with it the property of being an oxidising agent.

On the other hand, the to-be-expected homologues of Mn, metals to come between Mo and Ru and between W and Os, have not yet been discovered, and there is only the slightest reason for supposing such metals to exist. Further, Mn, in both its physical and chemical properties, shows the closest resemblance to the metals of the iron group, whereas it shows practically none to the halogens. Potassium manganate is not even similarly constituted to potassium chlorate.

A much better arrangement is to place Mn in the VIII.th group, which will then be—

Mn	Fe	Ni	Co
Ru	Rh	Pd	
Os	Ir	Pt	

This arrangement gives expression to the facts that Mn, Fe, Ni, Co are metals of similar appearance, mechanical properties, specific gravity, and melting-point; that their divalent simple and double salts are similarly constituted and isomorphous, *e.g.*, $MeSO_4,7H_2O$, $R_2SO_4MeSO_4,6H_2O$, &c.; that Mn, Fe, and Co all form alums and metallo- and metallicyanides. Mn shares this last property with Ru and Os, and its most highly oxidised salts, K_2MnO_4 and $KMnO_4$, are paralleled by K_2RuO_4, $KRuO_4$, and K_2OsO_4.

Further, a fuller examination of the properties of the metals of this group shows in many cases a regular gradation from Mn to Co in the top line and a corresponding gradation from Ru to Pd and from Os to Pt.

It is not necessary to assume the existence of a series of at present unknown elements to fill the vacant column in the VII.th group. This group is not alone in having only a single column of elements; the argon group bears it company in this respect.

The Chemical Laboratory,
L.C C. Paddington Technical Institute,
Saltram Crescent, W.

THE TECHNICAL DETERMINATION OF BENZENE IN ILLUMINATING GAS.

By D. A. MORTON.

The value of benzene vapour as a light producer in illuminating gas has led to its extensive use for enriching purposes, and its exact estimation in a simple way has become a matter of consequence.

Since 1 per cent only in coke oven gas gives a lighting value of more than twelve candle-power, while 1 per cent of ethylene gives less than one and one-half candle-power, there is a large difference in the lighting value of these constituents and their separate determination is necessary.

Although a number of methods have been proposed for the determination of benzene, and some of these requiring long and careful manipulation are quite exact, none appears to be satisfactory for use in technical work where a simple and rapid, as well as reasonably accurate, test is desired.

W. Misteli (*Journ. Gasbeleucht*, Sept. 9, 1905, p. 804), in a recent review, cites the method of Haber and Oechelhaeuser (*Ber.*, xxix., 2700) as being the only one suitable for testing small quantities of gas, yet even this method does not compare in rapidity and simplicity with the ordinary volumetric tests in technical analyses. The gist of the method is the absorption of the ethylene by bromine water and subsequent titration of the excess of bromine. Benzene vapours, the authors claim, while dissolving completely or partially in the bromine water, do not unite chemically with the bromine and hence do not affect the titration. Only by long contact is there a slight reaction with the benzene. The difference between the ethylene found and the total illuminants is taken as the percentage of benzene.

The method of Dennis and O'Neill, published in 1903 (*Journ. Am. Chem Soc.*, 1903, xxv., 503), in which the benzene vapours are absorbed by shaking the gas in a pipette with ammonium nickel nitrate solution of prescribed strength, is, unlike the preceding method, simple and rapid and suitable in these respects for technical use. The nickel method was used for a considerable time in this laboratory because, on account of its convenience and supposed accuracy, it was presumed to be suitable for the purposes here required. Nevertheless on a number of occasions the tests were found to be incorrect and consequently a more exhaustive investigation of its merits was finally carried out, with results of such interest that we give them in detail below.

Investigation of the Ammonium-nickel Nitrate Method.

The ammonium-nickel nitrate solutions for the experiments were made up according to the directions given in the original article (*loc. cit.*, p. 505). Both the regular solution and Geer's solution were tried, with identical results; and, since the solutions were made up by more than one analyst and at a number of different times, we cannot suppose the errors found in the tests to have been due to errors in preparing the solutions.

Following the directions of the authors in carrying out the tests, mixtures of benzene vapour and air were analysed, 100 cc. of the gas mixture being shaken three minutes in an absorption pipette with the ammonium-nickel nitrate solution, then three minutes in a second pipette with 5 cc. of 5 per cent sulphuric acid over mercury to remove ammonia fumes. The decrease in volume by this treatment indicates the percentage of benzene.

Table A shows the results obtained. The percentage of benzene present in each case was determined by absorption with fuming sulphuric acid as in the regular way for illuminants. Besides the percentage of benzene present, and that found by the ammonium-nickel nitrate test, the table gives the cubic centimetres of benzene vapour previously absorbed by the reagent, for this has a decided influence, as will appear.

A glance at the results of Table A shows that the absorbing solutions must be perfectly fresh to obtain results that are even approximately correct. In tests 2 to 6, although at most only a small quantity of benzene vapour had previously been absorbed, in no case has more than three-fourths the benzene actually present been found by the test. In 1, 100 cc. of air, shaken with the reagent and the 5 per cent sulphuric acid, has its volume *increased* to 101·1 cc.

If fresh ammonium-nickel nitrate solution and fresh 5 per cent sulphuric acid are used for each test (7 to 10) the results are better, though still too low by several tenths of 1 per cent. In technical works, where complete analyses have sometimes to be made as frequently as once an hour, refilling the pipettes with fresh solutions for every test is an inconvenience that is best avoided. An improvement has been made in the laboratory of the Detroit Solvay works, where the gas mixture is shaken three minutes in each of two ammonium-nickel nitrate pipettes, thus keeping the contents of the second pipette comparatively fresh for some time.

On further examination we find not only that the ammonium-nickel nitrate solution is an indifferent absorbent for benzene, but also that the absorbing power it does possess is due, *not to the nickel compound but to the water present*. That either water alone or dilute aqua ammonia gives practically the same results as the ammonium-nickel nitrate solution is shown in the table of comparative tests (Table B).

Table B shows results from a number of tests made under conditions as nearly identical as possible in all comparative cases. In I. fresh absorbing solutions were used. The gas taken for the test was air containing benzene vapour. One hundred cc. of the gas were passed into the absorbing pipette and shaken with the absorbent for the number of minutes indicated, drawn out and passed into a pipette of 5 per cent sulphuric acid to remove fumes, then back into the burette, allowed the usual time to drain, and measured. In II. the same conditions were observed except that the absorbing solutions were not fresh, having been used for the tests under I. In III. the gas in each case was shaken with the fresh reagent three minutes, then with 5 per cent sulphuric acid three minutes, the tests all being made with especial care.

Table C shows the results of strictly comparative tests of the absorbing power of ammonium-nickel nitrate solutions and pure water. In each case exactly 118 cc. of the absorbing solution were shaken for the time stated with 100 cc. of the gas and the unabsorbed residue drawn slowly back into the burette and measured. The gas was drawn back slowly to insure complete absorption of all ammonia fumes. (One hundred cc. of air passed into the fresh ammonium-nickel nitrate solution, shaken one minute and drawn back in the same way, re-measured exactly 100 cc.) Temperatures were the same, 18—19°, in all instances. In each case the gas tested was a mixture of air and a known quantity of benzene vapour.

From the results given in Table B we can draw no other conclusion than that in the determination by ammonium-nickel nitrate solution the benzene vapour is simply dissolved to a certain extent by the water in the solution—perhaps increased slightly by the ammonia in the case of the high percentages—but that the presence of the nickel compound has no appreciable influence whatever.

It would answer better to simply use fresh water each time as the solution for absorbing benzene, and, if used under proper conditions, good results could perhaps be obtained with this reagent. Nevertheless the use of a fresh solution, even water, for every test involves certain inconveniences and liabilities to error and would be objectionable in technical practice.

By the use of concentrated sulphuric acid for the benzene absorption a better method is obtained. This method is reliable and convenient, and the results by it are so comparatively accurate that we have no hesitation in recommending it for the technical analysis of coal gases.

TABLE A.

	Benzene present. Per cent.	Benzene found. Per cent.	Benzene vapour previously absorbed. Cc.
1.	0·0	−1·1	17
2.	0·5	0·0	17
3.	0·6	0·1	17
4.	0·6	0·3	1
5.	4·3	3·3	8
6.	4·7	3·2	12
7.	0·5	0·35	0
8.	1·0	0·7	0
9.	1·8	1·4	0
10.	4·2	3·7	0

TABLE B.

Absorbing solution.	Minutes shaken.	Benzene present. Per cent.	Benzene found. Per cent.	Benzene vapour previously absorbed. Cc.
		I.		
Ammonium-nickel nitrate	3	9·9	9·0	0
Aqua ammonia (sp. gr. 0·95)	2	9·9	8·8	0
Water	3	9·5	8·1	0
		II.		
Ammonium-nickel nitrate	3	9·9	8·0	9·0
Aqua ammonia (sp. gr. 0·95)	3	9·9	8·2	8·8
Water	3	8·4	7·4	8·1

III.

No. of test.	Benzene present. Per cent.	Benzene by ammonium-nickel nitrate. Per cent.	Benzene by water. Per cent.
1.	0·5	0·35	0·4
2.	1·0	0·7	0·8
3.	1·8	1·4	1·5
4.	4·15	3·65	3·4
5.	3·95	—	3·5
6.	4·15	3·6	3·35

TABLE C.

Series.	Absorbing solution.	Minutes shaken.	Benzene found. Per cent.	Benzene present. Per cent.	Benzene previously absorbed. Cc.
I.	Ammonium-nickel nitrate	2	6·1	7·2	0
	Water	2	6·0	7·2	0
II.	Ammonium-nickel nitrate	3	2·3	3·6	6
	Water	3	2·3	3·6	6
III.	Ammonium-nickel nitrate	2	0·4	1·0	0
	Water	2	0·4	1·0	0

TABLE D.—*Benzene-air Mixtures.*

No. of test.	Benzene present. Per cent.	Benzene found. Per cent.
1.	0·5	0·5
2.	0·6	0·6
3.	0·65	0·6
4.	1·9	1·9
5.	3·0	3·1
6.	3·6	3·55
7.	4·0	3·8
8.	4·5	4·35
9.	4·7	4·6
10.	7·8	7·7

TABLE E.—*Benzene-air Mixtures.*

No. of test.	Gas tested.	Benzene vapour previously absorbed.	Benzene present.	Benzene found.
		Cc.	Per cent.	Per cent.
1.	Benzene-air ..	55	1·9	1·9
2.	,, ..	120	3·0	3·1
3.	,, ..	150	4·5	4·3
4.	Air	55	0·0	0·0
5.	,, ...	100	0·0	0·0

TABLE F.—*Benzene-ethylene-air Mixture.*

No. of test.	Benzene present.	Benzene found.	Ethylene present.	Ethylene found.
	Per cent.	Per cent.	Per cent.	Per cent.
1.	0·55	0·85	9·5	9·5
2.	0·50	0·70	10·1	10·0
3.	0·50	0·65	4·8	4·7
4.	0·50	0·60	5·0	4·8
5.	1·0	1·05	9·95	10·1
6.	1·0	1·0	4·8	4·8
7.	1·0	1·05	5·0	5·0
8.	2·85	2·85	4·4	4·6
9.	3·0	3·0	4·5	4·7

TABLE G.—*Cubic Centimetres Ethylene Absorbed in Benzene Test.*

Ethylene present.	Benzene present (per cent).		
	0·0.	0·5.	1·0.
Per cent.	Cc.	Cc.	Cc.
1	0·05	0·00	0·00
2	0·10	0·05	0·00
3	0·10	0·05	0·00
4	0·15	0·10	0·05
5	0·20	0·10	0·05
6	0·25	0·15	0·10

The Concentrated Sulphuric Acid Method.

The marked solubility of benzene vapour in water (see Tables B and C) renders necessary certain precautions in sampling and handling the gas previous to the test. If taken over water, the sample bottle should be completely filled with the gas, driving out practically all of the water, as otherwise some of the benzene will be absorbed.

After the determination of the carbon dioxide in the gas, by absorption in strong caustic soda or potash solution in the usual manner, the benzene test is accomplished as follows. (Caustic soda solution dissolves benzene to only a very slight extent, and the error caused thereby is negligible).

The gas residue is passed into an ordinary simple absorption pipette containing concentrated sulphuric acid (sp. gr. 1·84) and shaken *vigorously* with this reagent for one minute, by which treatment the benzene vapours are absorbed. (Slight dilution of this acid does not detract from its efficiency, but the dilution should not exceed 2 per cent). The shaking is satisfactorily accomplished by giving a quick sharp motion to the pipette in such a way as to mix the contents thoroughly about twice per second, during the specified one minute. It is essential to shake vigorously with the sulphuric acid as directed, for the last traces of benzene are absorbed slowly and require thorough contact with the acid.

Experimental data on the conduct of concentrated sulphuric acid as an absorbent for benzene are given in Tables D to G.

Table D shows results obtained with mixtures of benzene and air. Good results are obtained even when more than 7 per cent of benzene—a very high amount—is present.

Table E gives results showing that the concentrated sulphuric acid can be used for a large number of tests without renewal. The benzene combines with the sulphuric acid and is not removed by air subsequently introduced.

Table F shows the action of concentrated sulphuric acid on benzene-ethylene-air mixtures. The benzene is determined by the concentrated sulphuric acid test; the ethylene immediately afterwards by fuming sulphuric acid in the usual way. In this table a slight defect in the method appears, due to the absorption of a trace of ethylene by the concentrated sulphuric acid. Higher homologues of ethylene would be absorbed to a greater extent than ethylene itseif. The error diminishes rapidly as the percentage of benzene increases, becoming practically nil when 1 per cent or more of the latter is present, and probably not exceeding 0·2 per cent in the case of any coal-gas.

Table G shows the cubic centimetres of ethylene absorbed by the concentrated sulphuric acid test, per 100 cc. of gas, having given the percentage of benzene and ethylene present. By use of these data correction for the error can be made when desirable.

Conclusions.

From the results obtained the unsatisfactory character of the ammonium-nickel nitrate method is apparent. As pure water absorbs benzene to practically the same extent as the ammonium-nickel nitrate solution, it appears that the method really depends on the solubility of benzene vapour in water, or ammoniated water, and that the presence of the nickel compound has no influence. The results by the method are inaccurate and vary widely according to the amount of benzene in the gas and the quantity already present in the absorbing solution.

Concentrated sulphuric acid, on the other hand, absorbs benzene vapour as readily as could be desired, and can be used for a large number of tests without renewal, giving as accurate results after a hundred tests as when first prepared. The defect due to the absorption of ethylene is insignificant, but may be easily corrected for (see Table G). Traces of the higher olefines, however, may give a value slightly too high for the benzene percentage, though this error, as shown by our tests of rich and lean gases from a variety of coals, must be small, if not inappreciable.—*Journal of the American Chemical Society*, xxviii., No. 12.

OBSERVATIONS ON THE

YELLOW MODIFICATION OF MOLYBDIC ACID.

By JOHN HOWARD GRAHAM.

INVESTIGATIONS have shown that the yellow crystalline substance depositing from solutions of ammonium molybdate is of composition $H_2MoO_4.H_2O$. It was noticed as early as 1876, identified in 1882, and a crystal measurement made in 1903. The following is an extract from the paper as presented.—ED. *Journ. Franklin Institute.*

Recently, while transferring ammonium molybdate solution from a stock bottle to smaller reagent bottles, I noticed on the bottom of the former a yellow crystalline incrustation, and there were some loose crystals. There is scarcely a chemist who has not noticed a yellow, yellowish white, or white deposit under similar conditions; but I have never observed one so uniformly yellow and homogeneous, and my curiosity led me to the following investigation, the results of which, I think, should prove of interest to everyone handling such solutions.

I removed as much of the crust as I could, crushed it carefully, so as to expose the individual crystals, and then washed with pure water to remove adhering solution. The material was then air-dried. Whenever I had noticed the deposits from solutions of ammonium molybdate, without any good reasons for my doing so, I considered them basic

or acid ammonium molybdates, that is, salts in which either ammonia or molybdic acid predominates. With such views in mind, qualitative tests were made with the following results :—

The yellow substance is very sparingly soluble in water, and the aqueous solution decomposes on concentration, affording a bulky white precipitate, very soluble in ammonia, and this ammoniacal solution deposits on evaporation white crystals of the molybdates of ammonia, several because as many kinds of crystals were observed. The white precipitate is undoubtedly molybdic anhydride. Another sample of our material was found insoluble in nitric acid, as might be suspected from the fact that it deposits after continuous standing from solutions strongly acidified with nitric acid. The aqueous solution is decomposed by nitric acid, giving the same milky-white precipitate which I consider molybdic anhydride. It is very soluble in hydrochloric acid, in fact excessively so, making the solution syrupy. Heated very gently, it yields water ; at a higher temperature it turns bluish in colour, and if the heating is continued without air access, it becomes yellow and finally white when cold, and shows indications of incipient sublimation. When heated to redness it sublimes completely, the sublimate having all the appearances of pure molybdic anhydride. The results so far could easily have been obtained with any ammonium molybdate. The question suggested itself:—Does it contain any ammonia ? A rather large sample of the material was boiled with strong caustic soda. I thought I noticed ammonia. Test paper impregnated with mercurous nitrate solution just turned faintly brown. My conclusions were, that if the substance was a molybdate, it must be of a very acid character. Examined under the objective of a microscope magnifying 85 diameters, the crystals appeared clear, well-defined, and prismatic. They were so small that I could not make out whether they were of the isometric or the monoclinic system. Later, I obtained larger crystals, and upon examining them, placed them in the monoclinic system.

With the foregoing facts in hand, literature was searched with the hope that light would be thrown upon the subject. We looked up molybdates, of course, and found nothing that would agree with our substance even qualitatively. A great number of molybdates of ammonia were described by Kämmerer (*Journ. Prakt. Chem.*, 1850, Series 1, xlix., 445) and Delafontaine (*Journ. Prakt. Chem.*, 1865, Series 2, xcv., 136), the information in many cases being meagre and uncertain. It might be of interest to note that Kämmerer estimated molybdic anhydride by reducing with hydrogen to constant weight, and weighing the molybdenum dioxide ; also by heating the salt with air access, adding drops of hydrochloric acid from time to time, and finally weighing the molybdic anhydride. The ammonia was determined by the well-known soda-lime method, the evolved gas being collected in hydrochloric acid, and finally weighed as platinum.

The next most logical proceeding was to determine the composition of the substance by estimating water, molybdic anhydride, and ammonia. The method used by Kämmerer, and suggested by Fresenius, that of reduction by hydrogen, was used. Fresenius says, to use a porcelain boat in a hard glass tube, and that the temperature should not exceed a dull redness. I tried this. The water of crystallisation passed over at a very low temperature, and, unless this is increased, no more water comes over. Heating to a dull redness, water resulting from the reduction of the molybdic oxide passes over. At the end of about two hours, the reaction has ceased. The material has suffered various changes of colour, yellow to orange, to blue, to black, and to steel-grey.

Rammelsberg states that the contents of the crucible are frequently grey below and brown above (*Pogg. Ann.*, cxxvii., 281 ; *Zeit. Anal. Chem.*, v., 203). What I obtained was uniformly grey, and the weighings of the supposed molybdenum dioxide gave percentages of molybdenum trioxide as follows :—60·97, 61·12, 60·53, 61·55, 61·95, 61·82, 61·02, 61·64.

Having taken all proper precautions, yet the results were anything but concordant. My attention was next given to the ammonia content. Samples of 1 grm. of material each were thoroughly mixed with finely-divided soda-lime, and heated in the usual combustion tube for that purpose. The ammonia was collected in hydrochloric acid, and was to have been determined as platinum. From two determinations I obtained such slight traces of the double chloride of platinum and ammonium that I had to consider the ammonia as a negligible trace. I was greatly surprised. I attributed the traces of ammonia to ammonium nitrate occluded in the crystals, and made the ferrous sulphate and diphenylamine tests for nitric acid. The former was altogether unsuccessful, for the former salt immediately reduced the solution and gave the intense blue due to the lower oxides of molybdenum. With the other reagent I first obtained a blue, due, I think, to nitrates, and after a time the solution became intensely blue, due again, I think, to reduction of the tri-oxide of molybdenum. Undoubtedly the ammonia is present in small traces as nitrate. So my yellow substance contains no ammonia in its composition. This directs me upon a new course. As to the water content, two samples of material heated in covered porcelain crucibles, with flames about one inch high and barely touching the bottom, gave results as follows by difference :—20·07 per cent and 20·03 per cent.

The ammonium molybdate solution from which the material was deposited was purchased from Baker and Adamson and guaranteed pure. There could be present in the yellow substance, therefore, no base but ammonia, and no acids other than nitric and molybdic acids. Since ammonia and nitric acid are present only in traces, we can consider them out of the question. The material therefore should contain nothing but molybdic acid and water, both of which were found and estimated. If the water is present by 20 per cent, there should be 80 per cent of molybdic anhydride. How shall we account for the discrepancy between 61 per cent about, as determined, and 80 per cent theoretical ? It could be possible that the contents of the boat were overheated. The supposed molybdenum dioxide did look too grey when compared with the colour by which it has been described—brown to black. It looked exactly like the metal molybdenum itself, and it is possible to obtain the metal under these conditions. In order to see if I could get a different result by regulating the temperature more carefully, I heated a sample by stages, intending to stop the operation when I obtained constant weight. With a very low flame I obtained a result which, calculated for molybdic anhydride, gave 85·05 per cent. The height of the flame was then increased so as to have it just touch the tube. The percentage dropped to 78·77. Evidently the crucial point was again overstepped. The following three determinations were made with the flame not quite touching the tube—a Bunsen flame of about 1½ inches. The contents of the boat after cooling were uniformly dull black and homogeneous throughout.

Result.—79·93 per cent, 79·73 per cent, 80·00 per cent, the mean of which is 79·93 per cent, and this added to the mean of the water determinations, 20·05 per cent, gives 99·93 per cent, corresponding to the formula $MoO_3.2H_2O$ or $H_2MoO_4.H_2O$.

References to this substance are few, yet they furnish substantially what I have enumerated above. I did not conceive of the substance being a modification of molybdic acid or I should have discovered earlier that the ground had practically been covered by others.

In the year 1876 Junck observed the yellow deposit. (*Zeit. Anal. Chem.*, xv., 290). He thought it was a metameric form of molybdic acid resulting from the action of light upon the solution. He made several experiments along this line.

Sergius Kern took notice of the deposit, and published notes concerning it in 1878 (*Zeit. Anal. Chem.*, xvi., 52).

In 1882 Millingk makes mention that the yellow precipitate is $MoO_3.2H_2O$, and gives a meagre description,

adding that it is soluble 0·5 grm. about in 1 litre of water (Gmelin-Kraut's "Handbuch," 1882, [2], II.).

Parmentier, 1882, makes quite a thorough study of it, and his observations as to its physical and chemical properties and composition agree quite closely with mine (*Comptes Rendus*, 1882, 839). The results of his analyses are :—

H_2O	19·96	19·95	19·94
MoO_3	80·04	80·05	80·06

Parmentier mentions that the crystals are monoclinic in form, and in 1888 Vivier confirmed this statement (*Comptes Rendus*, 1888, cvi., 601).

It was not until 1903 that the final work upon the substance was done. De Schulten (*Bulletin French Min. Soc.*, 1903, xxxvi.) prepared the yellow material according to the methods of Parmentier, acknowledging and confirming all his statements. He puts his solutions aside for years so as to obtain crystals large enough for measurement, and when he obtained some measuring 0·9 mm., 0·8 mm., and 0·8 mm. respectively along the axes *a*, *b*, and *c*, he uses them for this purpose. In his paper reporting the work, he makes a drawing of one of the crystals, which shows the following forms :—

Positive and negative pyramids and orthodomes; two prisms, clino-dome, ortho- and clino-pinacoids, and basal plane. The angle between the basal plane and the ortho-pinacoid is 89·19°, making the crystals appear at first glance as though they were cubes. They are clear, and the faces are good reflectors.

Yellow molybdic acid is so far an unimportant substance, a mere chemical curiosity, but yet its manner of formation and its occurrence are of interest, and it deserves that we know its properties sufficiently well to be able to identify it. —*Journal of the Franklin Institute*, clxiii., No. 1.

A NECESSARY MODIFICATION OF VOLHARD'S METHOD FOR THE DETERMINATION OF CHLORIDES.*

By M. A. ROSANOFF and ARTHUR. E. HILL.

1. *On the Determination of Chlorides.*

VOLHARD'S method for the determination of chlorides is well known. It consists in acidifying the given solution with nitric acid, adding a ferric salt (say iron-ammonium alum) as an indicator, precipitating the chloride with a measured but excessive amount of a standard silver nitrate solution, and without filtering out the silver chloride, determining the excess of silver nitrate by titration with a standard solution of ammonium sulphocyanate. As long as the solution contains any silver, the ammonium sulphocyanate produces only a white precipitate of silver sulphocyanate. When the silver is gone, the solution is coloured red by the sulphocyanate of iron.

A somewhat extensive experience in using this rapid method gradually forced upon us the feeling that in its present form it is inaccurate. The more carefully the titration is carried out, the less distinct the end-point often seems to be. A historical investigation showed that others have had similar experience with the method. Some time after the appearance of Volhard's first paper (*Journ. Prakt. Chem.*, 1874, ix., 217) Brügelmann reported (*Zeit. Anal. Chem.*, 1877, xvi., 1) that the end-point in question was indistinct, explaining it, however, on the assumption that it was the free nitric acid present that was destroying the colour by oxidising the sulphocyanate. The interfering factor was more clearly discerned by Drechsel (*Journ. Prakt. Chem.*, 1877, xv., 191; *Zeit. Anal. Chem.*, 1877, xvi., 351), who found that sulphocyanate of iron is decomposed by the silver chloride first precipitated according to the following equation : $Fe(CNS)_3 + 3AgCl = FeCl_3 + 3AgCNS$. He consequently recommended filtering out the silver chloride before titrating with sulphocyanate. Then appeared Volhard's exhaustive and final paper on the determination of silver and the halogens (*Liebig's Ann.*, 1878, clc., 8). Volhard, on the one hand, refutes Brügelmann's view and, on the other hand, maintains that the decomposition of dissolved sulphocyanates by solid silver chloride, pointed out by Drechsel, is too slow to interfere with the precision of the method. "Since," he says, "as mentioned, the decomposition of silver chloride by sulphocyanic acid or by a solution of ammonium sulphocyanate proceeds *quite slowly*, a liquid faintly coloured by iron sulphocyanate is but very gradually decolorised by silver chloride. . . . This renders it possible to determine, by means of sulphocyanate, the quantity of silver contained in a nitric acid solution in the presence as in the absence of silver chloride." Nevertheless, he urges extreme caution in looking for the end-point, that is, for the first appearance of a permanent coloration; for he had found that in the presence of some 0·4 grm. silver chloride the very faint light-brown coloration first produced by the sulphocyanate failed to be intensified by the addition of eight more drops, accompanied by thorough shaking.

At present, analysts are not in agreement as to whether the precipitated silver chloride interferes or not with the sulphocyanate titration. Thus, to Sutton "experience has proved that it is absolutely necessary to filter off the chloride and titrate the filtrate and washings" ("Volumetric Analysis," Philadelphia, 1904, footnote to p. 144). Similarly, in connection with a precise physico-chemical study Knüpffer found it necessary to filter off the silver chloride ("Chemisches Gleichgewicht und Elektromotorische Kraft" in *Zeit. Phys. Chem.*, 1898, xxvi., 266). He believes, however, that the action of silver chloride on sulphocyanates is "very slight" and that removing the chloride is necessary only in case of highly dilute solutions. *But the majority of chemists consider the removal of the chloride unnecessary in any case.* Thus, Treadwell ("Analytische Chemie," vol. ii., p. 510, Leipzig and Vienna, 1905) makes no mention at all of any possible interference by the silver chloride, nor does the United States Pharmacopœia refer to it. Mohr and Classen ("Lehrbuch der Chemische-analytischen Titrimethode," Braunschweig, 1886, p. 403) state explicitly that the removal of the chloride is unnecessary and recommend Volhard's method in its original form. Finally, to quote one more authority, Friedheim directs ("Leitfaden fur Quantitative Chemische Analyse," Berlin, 1897, p. 125) " . . . And now, without filtering off the silver chloride, or even taking pains to cause it to coagulate by shaking (or boiling), sulphocyanate solution is added immediately, with continual stirring." In a footnote he emphasises, with Volhard, the necessity of considerable training before the eye can discern the "true" end-point of the reaction.

In view of this conflict of statement, and of the value of a rapid method for determining chlorides, it seemed desirable to establish once for all, by systematic experiments, whether Volhard's method is reliable in its original form or requires modification.

The question to be answered was, Is the velocity of the reaction between solid silver chloride and dissolved sulphocyanates really as slow as it is generally supposed to be? While experience had taught us that it must be appreciable, special preliminary experiments soon indicated that it was astoundingly rapid; for instance, about a grm. of silver chloride shaken with an equivalent amount of iron sulphocyanate in dilute solution was all but completely transformed into silver sulphocyanate in a very few minutes. To obtain a reasonable percentage of change, and yet a reliable measurement of time, it seemed best to employ equivalent quantities of ammonium sulphocyanate and silver chloride and limit the time of the reaction to two minutes. The apparatus employed consisted of a cylindrical glass vessel with a wide delivery tube appropriately fused on near the bottom. The vessel was blackened on

* Presented before the New York Section of the American Chemical Society, December 7, 1906. From the *Journal of the American Chemical Society*, xxxix., No. 3.

the outside and the delivery tube was closed by a piece of wide rubber hose and a pinch-cock. The silver chloride was kept distributed throughout the volume of the solution by means of a stirrer driven by a gas engine. The temperature of the reacting mixture was about 28°, and it varied by scarcely one-tenth of a degree during the reaction. A good filter of glass-wool and the use of a suction-pump permitted of removing a clear sample of about 50 cc. for analysis in about three seconds. In each experiment, the silver chloride was prepared by precipitating, in a blackened flask, a known volume of standard silver nitrate solution with a slight excess of hydrochloric acid and carefully washing the coagulated precipitate by decantation. The precipitate was washed into the reaction-cylinder, water added to a 180 cc. mark, an equivalent amount of ammonium sulphocyanate solution (20 cc.) thrown in out of a test-tube, and the time noted. At the end of 120 seconds a sample was removed for analysis by opening the rubber hose of the delivery-tube directly over the glass-wool filter.

The analytical method employed was as follows:—An unmeasured volume of solution was precipitated by a known excessive amount of silver nitrate. After filtering, the excess of silver was determined in the solution with standard ammonium sulphocyanate, and an indicator of iron alum; this showed the total amount of silver precipitated. The mixed precipitate of AgCl and AgCNS was then transferred into an Erlenmeyer flask and boiled with an excess of concentrated nitric acid for three-quarters of an hour (Borcher's method). Thereupon water was added, the silver chloride filtered off, and the silver nitrate (from oxidised silver sulphocyanate) determined in the filtrate again by means of standard ammonium sulphocyanate and ferric salt; this showed the amount of silver originally precipitated as sulphocyanate.

Following are the results of three experiments:—

	AgCl.	NH_4CNS.	Volume.	Temperature.	Time.	NH_4CNS changed to NH_4Cl.
	Grm.	Grm.	Cc.		Seconds.	Per cent.
1.	0·286	0·152	200	28·2°	120	45·6
2.	0·286	0·152	200	28·4°	120	43·1
3.	0·286	0·152	200	28·3°	120	41·3
				Average		43

The agreement of the results is more than sufficient for our purpose. But if the astonishing amount of 43 per cent of sulphocyanate is destroyed by only an equivalent amount of silver chloride in two minutes, it must be expected that a large excess of the silver chloride (such as is present during a titration by Volhard's method) would destroy practically all the sulphocyanate in a few seconds. This was, in fact, shown by semi-quantitative experiments; amounts of silver chloride varying between 0·1 and 0·5 grm. were uniformly found to destroy the iron sulphocyanate formed by 2 to 10 drops of a N/15 NH_4CNS solution in from 5 to ten seconds. The following observation is specially convincing: 0·5 grm. of pure silver chloride was placed in 203 cc. of water in a bottle, and 2 cc. of a saturated solution of iron-ammonium alum were added; ½ cc. of a N/15 NH_4CNS solution was then rapidly introduced from a burette, the bottle stoppered, and the whole vigorously shaken for ten seconds. The solution, originally deep-red, was now practically colourless; an "end-point" given by ½ cc. of the reagent had disappeared in ten seconds.

In view of these facts, the following analytical results, obtained by Volhard's method in its original and modified forms respectively, will not appear surprising. First, a set of six determinations were carried out without filtering out the silver chloride (but changing somewhat the rate of stirring). The chloride solution employed was found gravimetrically to contain 2·324 grms. of chlorine per litre. Found by Volhard's method.

	Cl per litre in grms.	Relative error.
1.	2·256	−2·9 per cent
2.	2·277	−2·0 ,,
3.	2·299	−1·2 ,,
4.	2·324	— ,,
5.	2·322	−0·5 ,,
6.	2·276	−2·0 ,,

The same solution precipitated with an excess of silver nitrate and filtered from the silver chloride gave uniformly excellent results:—

	Cl per litre in grms.	Relative error.
1.	2·328	+0·17 per cent
2.	2·328	+0·17 ,,
3.	2·327	+0·13

The conclusion is plain; Volhard's method for the determination of chlorides must be modified by filtering out the silver chloride. While this modification diminishes somewhat the rapidity of the method, it is under all conditions indispensable.

(To be continued).

PROCEEDINGS OF SOCIETIES

CHEMICAL SOCIETY.

Ordinary Meeting, October 24th, 1907.

Sir WILLIAM RAMSAY, K.C.B., F.R.S., President, in the Chair.

MESSRS. J. V. J. Hayman, J. W. Shepherd, and C. H. Warner were formally admitted Fellows of the Society.

The PRESIDENT reminded Fellows of the loss which the Society had sustained since the previous meeting by the death of Sir William Henry Perkin, Dr. John Clark, Dr. August Dupré, and Mr. F. J. M. Page.

It was announced, also, that on the occasion of the Centenary Celebration of the Geological Society, the following address was presented:—

In the name of the Chemical Society we welcome the present opportunity of offering our warmest congratulations to the President, Council, and Fellows of the Geological Society of London on the occasion of its Centenary Celebration.

It is impossible to overestimate the value of the great work which your Society has accomplished during the past hundred years, both in laying the solid foundations of a new science and in helping to raise on these foundations the stately edifice of Modern Geology.

The connection between Geology and Chemistry has always been, and must ever remain, a very intimate one, and the early history of your Society shows that Chemists a hundred years ago fully recognised that their special branch of Natural Knowledge was destined to play an important part in elucidating those changes in the structure of the earth which fall within the special province of the Geologist.

This association between the two Societies is brought into further prominence by the fact that amongst the thirteen original founders of your Society, we find the names of no less than five celebrated chemists, viz., Arthur Aikin, William Allen, Humphry Davy, W. H. Pepys, and Richard Phillips; whilst within the first few years of your corporate existence the roll of your Fellows includes the names of Thomas Thomson, William T. Brande, Edward Turner, James Hall, W. H. Wollaston, J. F. Daniell, Charles G. Daubeny, and Alexander J. Marcet.

The advances in Modern Petrology, a sub-section of Geology which may be said to have been initiated by your Society, have demanded a still closer union between our respective branches of Science, and in the new ideas introduced within the last decade by the discovery of radio-

activity we see further indications that Physical Chemistry in the near future must influence many of the fundamental doctrines bearing on the age of the earth, and on the various changes which the earth has undergone within the period embraced by Geology.

Signed, on behalf of the Chemical Society,

WILLIAM RAMSAY, President.
ALEXANDER SCOTT, Treasurer.
M. O. FORSTER, } Honorary
ARTHUR W. CROSSLEY } Secretaries.
HORACE T. BROWN, Foreign Secretary.

Certificates were read for the first time in favour of Messrs. John Forbes Bell, Craigmillar, Edinburgh; Edward Joseph Day, M.D., M.R.C.S., L.S.A., Dorchester, Dorset; Frederick Harold Dupré, Mount Edgcumbe, Sutton, Surrey; Percy Vivian Dupré, A.C.G.I., Mount Edgcumbe, Sutton, Surrey; Francis Bridger Dutton, Birch Hall, Windlesham, Surrey; Thomas Rigby Greenough, B.A., Beechwood, Leigh; William Doge Hutchinson, B.A., Lythmore, Tennyson Road, Harpenden; Harry Ingham, M.Sc., 26, Hamilton Street, Bury; Herbert Marsden, B.Sc., Bramford, Ipswich; Herbert Frederick Sankey Marshall, High Street, Burwell; Gerald Hargrave Martin, Delce, Park Road, Wallington; John Edward Langford Moore, Walton Cottage, Loughboro' Park, S.W.; Charles Samuel Mummery, Christ's Hospital, West Horsham; Harold Ramsay Stobie, Clovelly, Craighall Gardens, Edinburgh; Frederick Thomas, B.Sc., 29, Fairhaven Road, St. Annes-on-the-Sea; Harold Munkman Timpany, M.Sc., St. Winifrede's Gardens, Shrewsbury; George Arthur Watson, A.R.C.S.I., 7, Roseneath Villas, Cork; Edward Wheeler, A.C.G.I., 113, Highbury Quadrant, N.; Robert Whymper, A.C.G.I., St. Clare, St. Mary's Road, Ditton Hill; Percy Williams, B.Sc., c/o The Wilhelmina Co., Pontianak, Dutch West Borneo; William John Wilson, A.C.G.I., 28, Windmill Street, Gravesend.

Of the following papers, those marked * were read:—

*192. "*The Constitution of Phenol- and Quinol-phthalein Salts: A Contribution to the Quinonoid Theory of Colour.*" By ARTHUR GEORGE GREEN and PERCY EDGAR KING.

Prof. Green gave an account of the following investigation which has been described in *Ber.*, 1906, xxxix., 2365; 1907, xl., 3724.

Green and A. G. Perkin have adduced evidence as to the constitution of phenol- and quinol-phthalein salts which cannot be reconciled with the indicator theory of Ostwald. On the other hand, the view that the appearance of colour during salt formation is due to a change of type from the lactone or triphenylcarbinol form to the quinonoid form has hitherto not met with general acceptance, largely owing to the failure of repeated attempts to obtain coloured carboxylic esters of these phthaleins.

The authors have now succeeded in preparing the coloured carboxylic esters, not only of the phthaleins themselves, but also of their mono- and di-methyl ethers. These esters, which are orange to red, are extremely unstable, being readily saponified, not only by weak acids or alkalis, but even by water. They form with acids, oxonium salts which are of a deeper colour than the free esters. Whilst the esters of phenolphthalein, $C_6H_4(CO_2Me)\cdot C\overset{C_6H_4:O}{\underset{C_6H_4\cdot OH}{=}}$, and of monomethylphenolphthalein, $C_6H_4(CO_2Me)\cdot C\overset{C_6H_4:O}{\underset{C_6H_4\cdot OMe}{=}}$, were obtained in the free state, and are more stable than their chlorides, the esters of quinolphthalein and of monomethylquinolphthalein could only be isolated in the form of the oxonium salts, thus, $C_6H_4(CO_2Me)\cdot C\overset{C_6H_3(OH)}{\underset{C_6H_3(OH)}{=}}O\cdot Cl$. The esters of dimethylphenolphthalein and of dimethylquinolphthalein (trimethyl derivatives) are only capable of existence as salts, a fact which agrees well with the representation of the chlorides as—

$$C_6H_4(CO_2Me)\cdot C\overset{C_6H_4:OMe}{\underset{C_6H_4\cdot OMe}{=}}<\overset{H}{Cl}$$

and—

$$C_6H_4(CO_2Me)\cdot C\overset{C_6H_3(OMe)}{\underset{C_6H_3(OMe)}{=}}O\cdot Cl.$$

The monomethyl esters of both phthaleins are soluble in alkalis, giving strongly coloured solutions similar to those of the phthaleins themselves, but not decolorised by an excess of alkali. On the other hand, the isomeric lactone ethers are colourless, and do not give coloured salts.

These facts disclose an exact parallelism between the esters and salts of these phthaleins and those of fluorescein and place the quinonoid structure of these substances almost beyond question.

DISCUSSION.

Dr. HEWITT remarked that in certain cases it was very difficult to assign a quinonoid constitution to coloured compounds. He had himself found that the colourless lactone of 2 : 4 : 2′ : 4′-tetrahydroxydiphenylacetic acid dissolves in alkalis with a colour extremely like that produced by phenolphthalein, but the colour is discharged on breaking the lactone ring. He had not, however, been able to devise any plausible quinonoid formula for the salts of the lactone.

Prof. GREEN, replying to Mr. Baly, said that the assumption of an oxonium hydrate group in the alkali salts of phenolphthalein was not a necessary deduction from his experiments, but was only advanced in order to give a clearer expression to the analogy in behaviour between these salts and those of quinolphthalein, the latter of which must contain an oxonium group.

Mr. Baly's statement that a quinonoid compound containing oxonium hydrate groupings would be colourless did not rest on any experimental evidence known to him.

The conclusion that the esters described were quinonoid compounds was in no way deduced from their colour, but was a necessary consequence of the experimental facts adduced in the paper, and depended especially on the proof that the methyl group was attached to the carbonyl and the chlorine atom in the ester chlorides to oxygen. These facts, especially in the case of the trimethyl ether of quinolphthalein, scarcely admitted of any other interpretation than that given.

*193. "*Ketene.*" By NORMAN THOMAS MORTIMER WILSMORE.

The gaseous substance produced by the action of a hot platinum wire on acetic anhydride, which was discovered by Dr. A. W. Stewart and the author (*Nature*, 1907, lxxv., 510), has been further examined. As a mean result, it was found that, on exploding one volume of the gas with excess of oxygen, there was a contraction of 1·09 volumes, and that the residual gas contained 1·97 volumes of carbon dioxide, whilst 2·08 volumes of oxygen had disappeared. The corresponding numbers for a gas having the formula C_2H_2O would be 1 : 1 : 2 : 2. A mean value for the density gave a molecular weight of 41·4, instead of 42. The gas has, however, not yet been obtained entirely free from acetylene and higher hydrocarbons. Its marked tendency to condense slowly, on standing, to a brown liquid is one of the chief difficulties in the way of its purification.

The substance combines directly with aniline to form acetanilide, with *o*-toluidine to form aceto-*o*-toluidide, with anhydrous liquid ammonia to form acetamide, and with ethyl and amyl alcohols to form the corresponding acetic esters. It also reacts vigorously with bromine, forming bromoacetyl bromide. As no by-products appear to be formed in these reactions, it may be inferred that the substance is a new anhydride of acetic acid, having the formula $CH_2{:}CO$ or $CH{:}C\cdot OH$, and, further, that it is the lowest member of the ketene series. With water, *ketene* gives chiefly acetic acid, but an aldehyde, probably glycollaldehyde, is formed at the same time. Ketene is also produced when an arc is made to burn under the surface of liquid acetic anhydride.

DISCUSSION.

The PRESIDENT suggested that a third possible formula for ketene would be , a substance having the same relation to acetylene as ethylene oxide has to ethylene. Such a compound might lend itself easily to polymerisation.

*194. "*Derivatives of the Multiple Ketene Group.*" By JOHN NORMAN COLLIE.

The group ·CH_2·CO· (which the author proposes to call the "*ketide*" group) can be made to yield by means of the simplest reactions a very large number of interesting compounds, all belonging to classes which are largely represented amongst the compounds obtained from plants.

Illustrations of this were given from the various published papers of the author. It was shown how by uniting more than one of these groups as in ethyl acetoacetate, $H[CH_2{\cdot}CO]_2OH$, or in dehydracetic acid, $H\,CH_2{\cdot}CO]_4OH$. "*polyketides*" are obtained, and from these by means of the simplest reactions, such as hydration, dehydration, oxidation, reduction, loss of carbon dioxide, or action of ammonia, complicated polyketide derivatives result. These are found to represent many of the various types of compounds found in plants.

This can be partly illustrated as follows :—

$H(CH_2{\cdot}CO)OH$ Acetic acid. $H[CH_2{\cdot}CO]_2OH$ Diacetic acid. $H\,CH_2{\cdot}CO]_4OH$ Tetra-acetic acid.

$H[CH_2{\cdot}CO]_4OH$ Tetra-acetic acid.

With acids, loss of $CO_2 + H_2O$ Dimethylpyrone.

With alkalis, loss of $CO_2 + H_2O$ Orcinol.

With NH_3, loss of $CO_2 + H_2O$ Lutidone.

Hydration Diacetylacetone. → Loss of water

Loss of H_2O from 2 mols. Benzene compound. → With NH_3 *iso*Quinoline compound.

Further loss of H_2O Naphthalene compound.

DISCUSSION.

Dr. M. O. FORSTER inquired what compounds, exactly, were to be classified as polyketides. The name naturally invited comparison with the words polymethylene and polypeptide, the significance of which was perfectly clear, and from that standpoint a polyketide would be a substance built up of the complex, $[\cdot CH_2{\cdot}CO\cdot]x$, with the necessary terminal groups or atoms. The application of the word in Prof. Collie's paper, however, was much more comprehensive, appearing to embrace such heterogeneous types as lactones, pyrone derivatives, benzenoid compounds, and substituted pyridines, and the speaker foresaw considerable danger in launching an entirely novel expression on chemical nomenclature without defining its scope more precisely.

*195. "*Production of Orcinol Compounds by the Action of Heat on the Sodium Salt of Ethyl Acetoacetate.*" By JOHN NORMAN COLLIE and EDWIN RODNEY CHRYSTALL.

When ethyl acetoacetate (78 grms.) is mixed with sufficient sodium ethoxide (4·6 grms. of sodium in 50 cc. of ethyl alcohol) to convert about one third of it into the sodium salt and the mixture heated, ethyl acetate, alcohol, and ethyl acetoacetate distil. On treating the viscous residue in the flask with hydrochloric acid, a crystalline compound separates, which is best purified by re-crystallisation from benzene (yield about 7·8 grms.) It has the composition $C_{16}H_{16}O_6$, and melts at 169°, $4C_6H_{10}O_3 = C_{16}H_{16}O_6 + CH_3{\cdot}CO_2Et + 2EtOH + 2H_2O$.

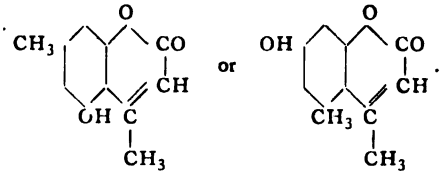
The new compound is soluble in aqueous sodium hydroxide with a deep yellow colour, but the colour changes to pale yellow on warming; acids precipitate from this solution an orange compound of high molecular weight, and alcohol is found in the residue. With sodium hydroxide and chloroform, it gives the orcinol reaction. With bromine, a compound of formula $C_{16}H_{15}O_6Br_3$, melting at 182·5°, is produced.

When warmed with 90 per cent sulphuric acid to about 130—140°, carbon dioxide is evolved, together with alcohol and acetic acid, leaving a compound of formula $C_{11}H_{10}O_3$ melting at 250°,—

$$C_{16}H_{16}O_6 + 2H_2O = C_{11}H_{10}O_3 + CO_2 + EtOH + C_2H_4O_2.$$

This compound is identical with a substance prepared by von Pechmann and Cohen (*Ber.*, 1884, xvii., 2188) from orcinol and ethyl acetoacetate.

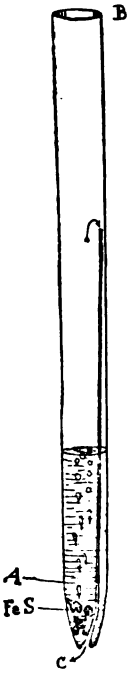
Its composition is either :—



The *monomethyl ether* (m. p. 146°) and the *monoacetyl* derivative were prepared (m. p. 198°).

196. "*A Simple Gas Generator for Analytical Operations.*" By JAMES MCCONNELL SANDERS.

The simple appliance described below has been found to be a convenient and practical substitute for the so-called "constant supply" apparatus of the "Kipp" type. It consists of a glass tube open at one end, and having a fine, almost capillary, tube fused into the other end, as shown in the figure.



The apparatus is charged, for example, for the preparation of hydrogen sulphide by dropping one or two small fragments of ferrous sulphide into the tube so that they lodge in the annular space (A), a few drops of dilute sulphuric acid are then allowed to run into the tube, and the mouth (B) closed with the forefinger. The apparatus may then be introduced into a test-tube or beaker and used as an agitator, the gas escaping by way of the fine interior tube and the orifice (C).

For quantitative work, a larger apparatus is used, and the mouth closed with a cork. For the preparation of a gas which requires the application of a gentle heat, the apparatus is allowed to touch the bottom of the test-tube while immersed in the liquid contents of the latter, and heat is applied to the test-tube itself.

After use, the generation of gas is instantly stopped by directing a stream of water from a wash-bottle into the interior, the outside is washed in the same manner, and the apparatus is then ready for use in a subsequent operation. The appliance has been in constant use in the Mexican Customs laboratories for the last five months, and in no case has it been found that the small inner tube showed any tendency to become clogged with precipitate.

(We are indebted to the author for permission to insert the woodcut illustrating this article).

197. "*Some Double Ferrocyanides of Calcium, Potassium, and Ammonium.*" By JAMES CAMPBELL BROWN.

The conditions of preparation and the properties of calcium potassium ferrocyanide and calcium ammonium ferrocyanide were explained. These salts have been analysed and their solubilities determined. The calcium potassium ammonium ferrocyanides resulting from the mixture of varying proportions of calcium chloride, potassium ferrocyanide, and ammonium chloride were described, and the conditions for the use of ammonium chloride and potassium ferrocyanide as a qualitative test for calcium were given.

198. "*Determination of Halogen in Organic Substances.*" By JAMES MOIR.

The new method described last year by the author (*Proc.*, 1906, xxii., 261) has been improved by adopting the Volhard method of back-titration with standard thiocyanate.

The contents of the crucible after heating are dissolved and treated with a crystal of bisulphite to reduce manganate. A measured quantity of standard silver solution is added, and the mixture is then acidified with nitric acid, heated to 70°, filtered through a Buchner funnel, using hardened paper, and the residue on the filter is extracted with hot dilute nitric acid. The filtrate is then cooled to 40°, and titrated with standard thiocyanate and iron alum.

Each cc. of N/10 silver solution, by difference, = 0·0080 grm. of bromine.

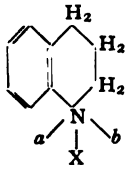
199. "*Racemisation by Alkali as Applied to the Resolution of r-Mandelic Acid into its Optically Active Isomerides.*" By ALEX. MCKENZIE and HERMANN AUGUST MÜLLER.

It was shown that, as a product of the fractional saponification of *l*-menthyl *r*-mandelate in ethyl-alcoholic solution, either a dextrorotatory or a lævorotatory mandelic acid mixture may be obtained from the same weight of ester, and using the same weight of alkali. The normal action is the formation of a dextrorotatory potassium salt; the formation of a lævorotatory potassium salt under the conditions quoted is abnormal.

Various methods of effecting the changes:—(1) *r*-Mandelic acid → *r*-mandelic acid and *l*-mandelic acid, and (2) *r*-mandelic acid → *r*-mandelic acid and *d*-mandelic acid were indicated.

200. "*The Optical Activity of Cyclic Ammonium Compounds.*" By FRANK BUCKNEY and HUMPHREY OWEN JONES.

Although it has been shown in a large number of cases that compounds of the type N*abcd*X can give rise to optical activity due to the asymmetric nitrogen atom, yet there is no well-established case of activity when the nitrogen atom forms part of a ring. It was stated previously (*Trans.*, 1903, lxxxiii., 1405) that substituted pyridinium compounds, quinolinium compounds, and tetrahydroquinolinium compounds of the type—



are all devoid of a plane of symmetry, and should be capable of giving rise to optical activity. Several compounds were then examined, but no evidence of activity was obtained.

The following fourteen compounds have now been examined: — 1-Methyl-*a*-picolinium-*d*-camphorsulphonate and *d*-bromocamphorsulphonate, methyl- and benzylquinolinium-*d*-camphorsulphonatesmethylkairolinium-1-acetate-*d*-camphorsulphonate and *d*-bromocamphorsulphonate, 1-methyl-1-ethyltetrahydroquinolinium-*d*-camphorsulphonate and *d*-bromocamphorsulphonate, 1-benzyl-1-ethyltetrahydroquinolinium-*d*-camphorsulphonate, benzylkairolinium-*d*-camphorsulphonate, *d*-bromocamphorsulphonate and tartrate, *n*-propylkairolinium-*d*-bromocamphorsulphonate, allylkairolinium-*d*-bromocamphorsulphonate. In the case of the last-mentioned compound only was there conclusive evidence of the existence of optical activity, the *l*-base *d*-acid salt was the less soluble, and had $[M]_D = 198°$, and the *d*-base *d*-acid had $[M]_D = 343°$. The iodide was recovered in small quantity only, but was decidedly active.

201. "*The Action of Phosphorus Pentachloride on Hydroxytrimethylsuccinic Ester. 1:2-Dimethylcyclopropane-1:2-dicarboxylic Acid (1:2-Dimethyltrimethylene-1:2-dicarboxylic Acid).*" By HERBERT HENSTOCK and BERTHA E. WOOLLEY.

The authors have examined the chief chemical and physical properties of 1:2-dimethyl*cyclo*propane-1:2-dicarboxylic acid (1:2-dimethyltrimethylene-1:2-dicarboxylic acid), the optical properties of its diethyl ester having been investigated for them by the late Sir William Perkin. The object of the work was to determine whether this constitution, which was assigned to the acid by Paolini (*Gazzetta*, 1900, [2], xxx., 497), is the correct one, since, if its saturated cyclic character were proved, an important difference is indicated in the behaviour of two so nearly allied substances as bromotrimethylsuccinic anhydride (which yields methylenedimethylsuccinic acid) and chlorotrimethylsuccinic ester when the hydrogen haloid is removed from the molecule. The authors' work confirms that of Paolini.

On the elimination of the hydrogen haloid from chlorotrimethylsuccinic ester, 1:2-dimethyl*cyclo*propane-1:2-dicarboxylic acid is formed.

202. "*The Condensation of Acetaldehyde and its Relation to the Biochemical Synthesis of Fatty Acids.*" By HENRY STANLEY RAPER.

It has been suggested that the formation of fatty acids, in animals, from carbohydrates depends, firstly, on a break-down of the carbohydrate to yield, amongst other products, acetaldehyde, and, secondly, on the condensation of the acetaldehyde leading to the formation of the higher fatty acids. The object of this investigation was to determine whether acetaldehyde on condensation yields the straight-chain compounds which would be necessary for the production of the higher fatty acids, as previous observations on the condensation of aldehydes point to the formation of compounds with branched-chains.

This objection to the above hypothesis has been partly removed, for it has been found that β-hydroxybutyraldehyde, the first product of the condensation of acetaldehyde, on further condensation yields an aldehyde contalning eight carbon atoms united in a straight-chain.

203. "*The Influence of Solvents on the Rotation of Optically Active Compounds.* Part X. *Effect of the Configuration and Degree of Saturation of the Solvent.*" By THOMAS STEWART PATTERSON, ANDREW HENDERSON, and FRANK WALTER FAIRLIE.

Solutions of ethyl tartrate in ethyl fumarate, ethyl maleate, and ethyl succinate were examined as regards rotation. Fumaric and maleic esters were found to have much the same effect, which is greater than the effect of succinic ester. The results were discussed from the point of view of combination of solute and solvent.

204. "*Para-toluidine Monohydrate.*" By JAMES WALKER and HEATHER HENDERSON BEVERIDGE.

p-Toluidine crystallises from water and from aqueous alcohol as a monohydrate which melts at about 41·5°, the melting-point of the anhydrous base being 43·5°. The monohydrate effloresces in the air, but, on the other hand, the anhydrous base absorbs water from air saturated with moisture, and is converted into the monohydrate. In contact with liquid water, the anhydrous base is converted into the monohydrate at all temperatures up to the melting-point of the latter. The pressure of water-vapour over the monohydrate at the ordinary temperature is somewhat more than half that of liquid water.

205. "*Hydrates of some Quaternary Bases.*" By DAVID COWAN CRICHTON.

Solutions of tetraethylammonium hydroxide, tetrapropylammonium hydroxide, and trimethylsulphine hydroxide were prepared from the corresponding chlorides by means of potassium hydroxide (compare Walker and Johnston, *Trans.*, 1905, lxxxvii., 955).

A *tetrahydrate* and a *hexahydrate* of tetraethylammonium hydroxide were described. When the tetrahydrate is made to lose water at the ordinary temperature, the base decomposes with formation of triethylamine, ethylene, and water.

A *heptahydrate* of tetrapropylammonium hydroxide was separated by cooling the aqueous solution in a freezing mixture. This hydrate melts when raised to the ordinary temperature.

Attempts to prepare a crystalline hydrate of trimethylsulphine hydroxide were unsuccessful.

206. "*Two Volumetric Methods for the Determination of Chromium.*" By ARNOLD WILLIAM GREGORY and JAMES MCCALLUM.

The authors have modified the persulphate method for the estimation of chromium in iron and steel, with the object of obtaining accurate results in a minimum time.

In the presence of manganese, the permanganic acid, formed simultaneously with the chromic acid, is reduced, either by the addition of a little ammonium chloride or by means of hydrogen peroxide.

The chromic acid formed is titrated with ferrous sulphate solution of known strength.

A method of oxidising the chromium with sodium bismuthate was also described. It is found to give very satisfactory results.

NOTICES OF BOOKS.

India-Rubber and its Manufacture. By HUBERT L. TERRY, F.I.C. London: Archibald Constable and Co., Ltd. 1907.

IN this book we have a pleasantly written account of the properties and uses of india-rubber. Its production is described in detail, and the characteristics of the chief rubbers of commerce are treated in an interesting manner. No attempt is made to go deeply into the chemical nature or properties of rubber, though some allusion is made to the determination of its formula and to the action of certain reagents upon it. The process of vulcanisation is treated from the practical point of view, and the methods of manufacture of mechanical goods are described sufficiently fully to enable the reader to get a grasp of the main outlines of each process, but no attempt is made to go into minute details relating to manufacture, which only the specialist would require and appreciate. The making of tyres is given a chapter to itself, and the gutta-percha and balata industries are also considered. As a very readable contribution to the vast branch of literature which is issued for the benefit of the educated and intelligent general public, who are more concerned with a wide than a deep knowledge, this book has every claim to regard. It is excellently printed and got up, and well provided with illustrations.

Memento du Chimiste. ("Chemist's Memorandum Book.") By A. HALLER and CH. GIRARD. Paris: H. Dunot et E. Pinat. 1907.

THIS collection of tables and data relating to pure and applied chemistry is a considerably enlarged edition of the "Agenda du Chimiste," which was issued annually some years ago. The first chapters contains numerical tables of physical constants, thermochemical data, and logarithmic tables, and Chapter II. describes the analysis of simple substances and mixtures for inorganic acids and bases; spectroscopic data are included in this part, and a tabular list shows the most important properties, including the solubilities at different temperatures, of a very large number of inorganic and organic substances. In Chapter III. the analysis of foods and a variety of technical products is treated, and it will thus be seen that the book contains a great deal of information, which is moreover arranged in a very handy form. The smallness of the print would make its constant use very trying, but on the other hand, in spite of the amount of matter it contains, the volume is by no means of an unwieldy size.

A Course of Practical Organic Chemistry. By T. SLATER PRICE, D.Sc., Ph.D., F.I.C., and DOUGLAS F. TWISS, M.Sc., A.I.C. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1907.

THE descriptions of methods of preparing organic compounds given in this book are very clear and explicit, and every help is given to the student, who, as one of a large class, is working with but little assistance from a teacher. The book completely covers the syllabus of the Board of Education Examinations, Stages I., II., and III., and also of the B.Sc. degree, and it is divided into three parts, each of which contains the subjects of one stage; although more preparations are described than each student will probably find it practicable to carry out, an excellent experimental course can easily be drawn up by making suitable selections of typical preparations. Methods of testing for various substances and groups of substances are included, and a good systematic scheme of identification should give the student great assistance in this difficult branch of his work. The difficulty of arranging a course of preparations for a beginner, in which he is not obliged to make use of substances of complex structure with which he is not acquainted, in order to prepare the simpler compounds, is to a certain extent met by describing first the purification of ethyl alcohol from methylated spirits or spirits of wine, and then dealing with the preparation of those compounds for which ethyl alcohol can conveniently be used as a starting point. This plan enables the student to do the experiments which require least knowledge and skill first, and at the same time helps him to keep in mind the genetic relations of the substances he is dealing with. The theoretically perfect arrangement has had to be abandoned in some cases, but on the whole the authors have proved very successful in the general plan as well as in the minor details of the book.

CORRESPONDENCE.

ALUMINIUM CARBIDE.

To the Editor of the Chemical News.

SIR,—In the CHEMICAL NEWS for November 15 (vol. xcvi., p. 246) an abstract of a paper on the "Preparation of Aluminium Carbide," by C. Matignon, was given.

We have been working for some time past on the reaction between aluminium and carbon, and have obtained the carbide from wood charcoal, from sugar carbon, and from certain hydrocarbons.

When the carbon and aluminium are present in sufficiently fine powder, the reaction is an exothermic one, and may be started by igniting a portion with a fuse of Mg and BaO_2; but as the reaction proceeds best when carried out in the open air, it is probable that the temperature of the burning Al enables the reaction to proceed, but when the action is once started and the air shut off, the reaction proceeds throughout the mass, which becomes red-hot.

The resulting carbide contains both alumina and aluminium nitride, and gives off H, CH_4, and a very small quantity of a gas smelling of acetylene. This could not have been more than 0·2 per cent of the whole, as this was the diminution with fuming H_2SO_4.

In contact with water the evolution of gas is slow, and in one experiment the evolution of gas has continued for over sixteen days, and is still continuing.

We are preparing aluminium carbide under varying conditions, with a view to discovering whether, at comparatively low temperatures, another carbide can be prepared. —We are, &c.,

HENRY R. ELLIS,
FRANK E. WESTON.

Chemical Laboratory,
The Polytechnic, Regent Street, W.,
November 19, 1907.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlv., No. 18, October 28, 1907.

Iodomercurates.—A. Duboin.—When ferrous iodide and mercuric iodide are dissolved in water and the mixed liquids allowed to stand in presence of iron, on evaporation crystals of $FeI_2.2HgI_2.6H_2O$ are obtained. If aluminium iodide is substituted for ferrous iodide, the resulting crystals contain oxygen, and have the formula $HgO+2AlI_3.3HgI_2.15H_2O$. A similar oxyiodide of aluminium and silver can be prepared by dissolving silver iodide in aluminium iodide. Its formula is $2AlI_3.5AgI.2AgO.13H_2O$.

Colloidal Solution of Arsenic.—V. Auger.—The reduction of a hydrochloric acid solution of arsenious anhydride with an aqueous solution of hypophosphorous acid in presence of concentrated alcohol at a temperature below 0° gives a yellow powder, which on drying turns red-brown, and which possesses the property of dissolving immediately in dilute soda, giving a brown colloidal solution. This solution is stable even on boiling, but oxidises rapidly in air, giving arsenite. Alcohol, soda, and potash in excess precipitate brown flakes, soluble in water. Dilute acids, even acetic acid, and all soluble salts precipitate from it brown flakes which are insoluble both in water and in dilute alkalis. When the solution is purified, either by dialysis or by precipitating with alkali and washing with concentrated alkali, a solution is obtained which is free from alcohol, but it has not yet been found possible to free it from traces of phosphorus and of alkali. The author is not at present certain whether the presence of phosphorus is necessary in order that this modification of arsenic may be soluble in alkalis.

Sources of Error in the Determination of Phosphorus in Iron, Cast-iron, and Steel.—G. Chesneau.—In determining the phosphorus in iron by Carnot's method of double precipitation with ammonium molybdate, it is necessary to use a very large excess of the latter reagent, since ammonium phosphomolybdate is soluble in ferric salts, and the following state of equilibrium results:—Am. phosphomolybdate + ferric sulphate $\rightleftharpoons$ ferric phosphomolybdate + am. sulphate, unless a large excess of molybdic acid and ammonium salts is present. In order to avoid loss by washing the ammonium phosphomolybdate, it is best to use, not water containing nitric acid or ammonium nitrate, but pure water. Ammonium nitrate, which in presence of ammonium molybdate renders the precipitation of ammonium phosphomolybdate more complete, dissolves the latter when no ammonium molybdate is present. Acid ammonium molybdate, which is formed when ammonium molybdate is heated for some time above 60°, is soluble in pure water and in water containing nitric acid, but is re-precipitated by ammonium nitrate. Thus if in order to effect complete precipitation the liquid containing phosphoric acid and ammonium molybdate is heated for some time, and thus some acid molybdate is precipitated with the phospho-compound, it is useless to attempt to purify the precipitate by again dissolving in ammonia and acidifying, for the acid molybdate is again partially precipitated by the action of the nitrate produced by the neutralisation of the ammonia. It is therefore best to keep the temperature of the liquid fairly low in order to avoid this error.

MISCELLANEOUS.

National Physical Laboratory.—Mr. Guy Barr, B.A., of Christ's College, Cambridge, has been appointed to an Assistantship in the Metallurgical and Chemical Department of the Laboratory.

Physical Society.—It is announced that the Third Annual Exhibition of Electrical, Optical, and other Physical Apparatus will be held at the Royal College of Science, South Kensington, on Friday evening, December 13th, from 7 to 10 o'clock.

Finsbury Technical College Old Students' Association.—The success which attended the Dinner held in December last has encouraged the council to make arrangements for a similar gathering before the close of the present year. The Second Annual Dinner will take place on Wednesday, December 11, at the Criterion Restaurant, Piccadilly Circus, W., at 7 p.m. for 7.30 o'clock, when the Chair will be taken by Mr. C. G. Redfern, F.C.I.P.A., &c., President of the Association. The cost of the tickets will be five shillings, exclusive of wine. Any Old Students (Day or Evening) should communicate with one of the following:—S. E. GRITTOS (Mechanical), Talfourd Cottage, Reigate, Surrey; ERNEST W. MOSS (Electrical), 20, Huddleston Road, Tufnell Park, London, N.; FRANCIS H. CARR (Chemical), "Kelvin," Church Avenue, Sidcup, Kent.

MEETINGS FOR THE WEEK.

MONDAY, Dec. 2nd.—Royal Institution, 5. General Monthly Meeting.
—— Society of Arts, 8. (Cantor Lectures). "Theory of the Microscope," by Conrad Beck, F.R.M.S.
—— Society of Chemical Industry, 8. "Estimation of Naphthalene in Coal-gas and in Spent Oxide of Iron," by C. J. Dickenson-Gair. "Influence of Formal on the Properties of *Fustrum elastica*," by P. Schidrowitz and F. Kaye. "Polarimetric Determination of Sucrose," by F. Watts and H. A. Tempany. "Niam Fat," by J. Lewkowitsch.

WEDNESDAY, 4th.—Society of Arts, 8. "Old Age Pensions," by Sir Edward W. Brabrook, C.B.
—— Society of Public Analysts, 8. "Volumetric Determination of Reducing Sugars" and "Determination of Invert Sugar in presence of Varying Amounts of Cane-sugar," by A. R. Ling and T. Rendle. "Quantitative Separation of Barium from Strontium," by Miss Zelda Kahan. "Action of Dimethyl Sulphate (Valenta's Reagent) upon Oils of the Aromatic and Aliphatic Series" and "Titration with Permanganate in presence of Hydrochloric Acid," by T. W. Harrison and F. M. Perkin. "Routine Methods for the Bacteriological Examination of Water," by A. R. Tankard.

THURSDAY, 5th.—Chemical, 8.30. "Affinity Constants of Bases as Determined by Methyl-orange," by V. H. Veley. "Velocity of Reduction of the Oxides of Lead, Cadmium, and Bismuth by Carbon Monoxide, and the Existence of the Sub oxides of these Metals," by F. J. Brislee. "Relation between Unsaturation and Optical Activity—Part I., The Menthyl and Bornyl Esters of β-Phenylpropionic, Cinnamic, and Phenylpropiolic Acids," by T. P. Hilditch. "Constituents of the Essential Oil of Nutmeg," by F. B. Power and A. H. Salway. "Methyl Ethers of some Hydroxy-anthraquinones," by A. G. Perkin. "Colouring-matters of the Stilbene Group—Part IV., The Action of Caustic Alkalis upon Paranitrotoluene and its Derivatives," by A. G. Green, A. H. Davies, and R. S. Horsfall. "Replacement of Alkyl Radicals by Methyl in Substituted Ammonium Compounds," by H. O. Jones and J. R. Hill.

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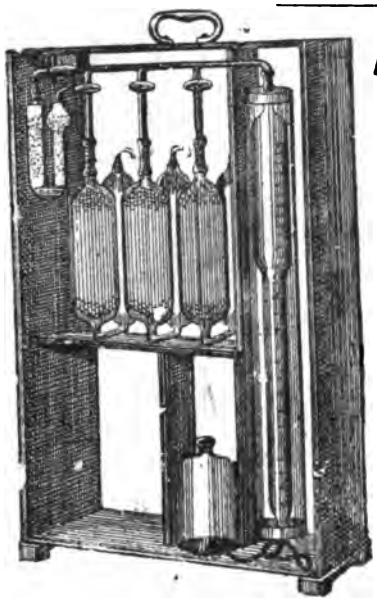

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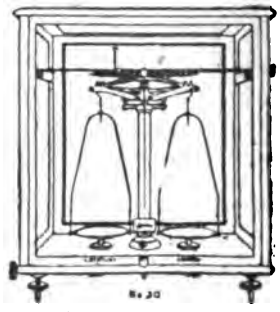

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THE CHEMICAL NEWS.

VOL. XCVI., No. 2506.

A NEW ELEMENT, LUTECIUM, OBTAINED BY SPLITTING UP MARIGNAC'S YTTERBIUM.

By G. URBAIN.

IN the separations of the elements of the yttrium group, I have always observed that ytterbia gives the most soluble salts. The method which seems to me the best for the preparation of this substance, free from yttria, erbia, and thulia, is the crystallisation of the nitrates (G. Urbain, *Bull. Soc. Ch.*, 1905, xxxiii., 739; *Journal de Chemie Physique*, 1906, iv., 31; "Extract from a Communication to Sir William Crookes," May 5, 1906, *Proc. Royal Soc.*, 1907, lxxviii., 154). In 1905 by this method I obtained 50 grms. of raw ytterbia, answering to Marignac's description (*Comptes Rendus*, lxxxvii., 578).

I propose in this preliminary note to describe shortly the researches which I have been carrying on since then.

In order to determine the atomic weight of ytterbium we are restricted to the analysis of the sulphates of similar products. It seemed to me to be necessary to subject the ytterbia to systematic fractionation in order that I might be sure that its atomic weight and its spectral characteristics were constant.

For this purpose I subjected the nitrates to fresh fractional crystallisations in nitric acid of density 1·3. Thus I obtained, after a very tedious series of fractionations, extending to 22 consecutive fractions, a series of products, the absorption spectra of which I examined first. The first fractions, numbers 9 to 16, showed faintly absorption bands which alone revealed the presence of thulium. I eliminated these fractions. The other fractions which might be considered to be pure ytterbium were transformed into sulphates and analysed.

Far from being constant the atomic weights varied, gradually increasing from 169·9 for fraction 17 to 173·8 for the last fraction, number 31 (see Note). Such a large variation is sufficient to show the complexity of ytterbium.

(NOTE. — For this first approximation I took O = 16, H = 1, S = 32. These numbers would be increased by about 0·17 if in the calculations I had taken O = 16, H = 1·008, S = 32·06. It may be mentioned that the atomic weight of thulium cannot be 171. It is undoubtedly below 168·5).

I tested the final products of my fractionations for thorium. By the very effective method of Wyrouboff and Verneuil (the action of oxygenated water upon the solution of the neutral nitrates), I succeeded in separating from the earths with the highest atomic weights about a twenty-thousandth of thoria, which could have no influence upon my measurements.

By the arc spectra method I was not able to detect the presence of any impurity in my products thus purified, and there is no doubt that my ytterbia was not a mixture of several constituents.

By photographing on the same plate one above the other the arc spectra of the extreme members of this fractionation, I detected in the spectrum of the last fraction (No. 31) many lines, mostly well marked, which could not be seen in the first fraction (No. 17), or which were very faint in it. Conversely, fraction 17 showed some not very strong lines which were absent in No. 31 and which were probably attributable to thulium. Apart from these lines the two spectra showed a great number of common lines of the same order of intensity. These lines are those which characterise the bulk of the original material, the impurities of which (thulium and the new element) accumulated, the former in the first and the latter in the last of my fractions.

Then I compared the spark spectra of my earths. The differences detected by this method of observation were much clearer than in the case of the arc spectra.

1. The lines in Table I. are the spark spectrum lines, attributable to thulium, which I detected in the fractions of low atomic weight (least soluble nitrates).

TABLE I.

2869·3	Faint.	3362·7	Fairly strong.
2899·9	Medium.	3425·7	,,
2962·5	,,	3441·6	,,
3050·9	Faint.	3461·9	,,
3131·4	Fairly strong.	3624·5	Faint.
3151·2	Medium.	3712·5	,,
3173·0	,,		

2. The lines in Table II. are the characteristic lines of the new element. They may very easily be detected in the fractions of high atomic weight (most soluble nitrates). They are either found exclusively in these fractions or else are much strengthened in them).

TABLE II.

*2701·8	Very strong.	3171·5	Fairly strong.
*2754·2	,,	*3183·5	Medium.
*2798·3	,,	3191·9	,,
*2847·6	,,	*3198·2	Strong.
2895·0	,,	*3254·5	Very strong.
*2900·4	,,	3275·5	Fairly strong.
*2911·5	,,	*3312·4	Strong.
*2951·8	,,	*3359·8	,,
*2963·5	,,	*3376·7	,,
2970·0	,,	*3385·6	Fairly strong.
*2989·4	Medium.	*3397·2	Very strong.
3020·7	Very strong.	*3472·6	,,
*3056·8	,,	*3506·8	,,
3058·0	,,	3554·6	,,
*3077·7	,,	3568·0	Strong.
*3080·3	Medium.	3624·1	,,
3118·6	,,	3647·9	,,

The lines marked with an asterisk are the most characteristic of the arc spectrum.

For the limits between which my measurements extend these 34 lines constitute the relatively complete spark spectrum of the new element. (None of these lines are due to scandium, thorium, erbium, thulium, yttrium, or to any common element or rare earth, except the old ytterbium).

I propose lutecium, Lu, derived from the old name of Paris, for the name of this element.

3. The other lines, included between the same limits, and enumerated in the spark spectrum of ytterbrium, recently described by Sir W. Crookes, from one of my old preparations (*loc. cit.*), characterise the bulk of the old ytterbium. I propose to give this earth the name neo-ytterbium, Ny, in order to avoid confusion with Marignac's element.

4. The first spectrum of the old ytterbium was described by Lecoq de Boisbaudran (*Comptes Rendus*, 1879, lxxxviii., 1342), to whom Marignac had sent his new earth. It was a band spectrum. When I examined the chlorides of the extreme members of my fractionation by Lecoq de Boisbaudran's method, I noticed that in the earth of low atomic weight (neo-ytterbium) Lecoq de Boisbaudran's γ band was absent. On the other hand, in the earths of high atomic weight, which are very rich in lutecium, this band γ is more marked than the other bands of the spectrum.

The bands α (from $\lambda = 559$ to $\lambda = 552$) and β (from $\lambda = 576$ to $\lambda = 568{\cdot}5$) are thus probably characteristic of neo-ytterbium, and the band γ (from $\lambda = 517{\cdot}5$ to $\lambda = 513$) of lutecium.

To summarise the observations I have described here, Marignac's ytterbium is a mixture of two elements, neo-ytterbium and lutecium. The atomic weight of neo-ytterbium cannot differ much from 170, and the atomic weight of lutecium is not much above 174.

I may mention that Demarçay (*Comptes Rendus*, 1900, cxxxi., 387) denoted by θ an element characterised by lines 4008·2 and 3906·5. He regarded it as distinct from thulium, and included between erbium and ytterbium. I was not able to detect these lines, obtained by the use of a special coil, either in my spark spectra nor in my arc spectra.

Moreover Auer von Welsbach (*Lieb. Ann.*, 1907, cccli., 464) has quite recently announced that by the fractionation of the double oxalate of ammonium and ytterbium he has detected spectral variations which he has not further defined. He did not give any measurements of the lines which he has observed between λ 7000 and λ 5000, and did not specify the elements which he supposes exist in the old ytterbium.—*Comptes Rendus*, 1907, cxlv., 759.

THE MOTHER SUBSTANCE OF RADIUM.

By OTTO HAHN.

As our knowledge of the nature of radio-active phenomena has grown, we have reached the conviction that even radium, which is apparently unchangeable, cannot keep its activity for ever, but that in course of time it must be converted into another inactive product.

Different views are at present held regarding the time which radium takes to undergo this change. The highest value for the decay period—the time in which a given quantity of radium decays to one-half—is 2600 years.

Owing to the great age of the solid crust of the earth, radium would have disappeared long ago, even if the whole earth had consisted of it alone, if we did not suppose that radium itself is continually formed afresh.

This supposition has been fully confirmed. The parent substance of radium is undoubtedly uranium, which undergoes a far slower transformation. It is also certain that one or more intermediate products must exist between uranium and radium, and thus uranium, or rather the so-called uranium X, cannot be the immediate mother substance of radium. A great many investigators have for some time been engaged in the search for this intermediate product.

At the end of 1906 Boltwood (*Phys. Zeit.*, vii., 915) announced that he had succeeded in showing that actinium, which had then been known for some time, was the mother substance. An actinium solution prepared by Boltwood undoubtedly showed an increase in the radium present in it after some months.

Shortly afterwards Rutherford (*Nature*, lxxvi., 126) proved that it was not the actinium itself, but an unknown product occurring with actinium, which produced radium. Giesel, Soddy, Meyer, and v. Schweidler all showed that actinium itself could not be the mother substance.

In a letter to *Nature* (September 26th, 1907) Boltwood described new experiments, confirmed Rutherford's result, and also stated that the hypothetical substance followed the reactions of thorium, and thus must be able to be easily separated, by the aid of these characteristic reactions, from actinium, which resembles lanthanum. In a letter to *Nature* (October 10th), he confirms his supposition, and states that the new substance emits α-rays of a low penetrative power. The product is thus proved to be a new element; Boltwood calls it "ionium."

In reference to this subject I wish to report shortly on experiments which were not quite concluded when Boltwood's statements were published, but which in another perfectly independent way showed that the mother substance of radium follows the chemical reactions of thorium, and can thus be separated with the latter from minerals containing uranium.

In the investigation of a new intermediate product in thorium, which I called mesothorium, I noticed that older "pure" thorium preparations contained relatively large amounts of radium. This was peculiar, for the substance used for the preparation of the thorium, monazite sand, contains only very small amounts of uranium. Naturally only a very small amount of radium corresponds to the small amount of uranium, and this must have been separated from the thorium in the complicated process of preparing pure thorium salts.

Some months ago I therefore began a systematic examination of different old pure thorium preparations to determine the amount of radium they contained. A weighed quantity of pure nitrate was dissolved in pure water, boiled to remove all the radium emanation, and then corked up in a little flask. After a sufficiently long time the contents of the flask were again boiled, the gases were collected in a burette, and some time after, when the thorium emanation had decayed, blown into a suitable electroscope. By comparison with an accurately known quantity of radium under the same conditions in this way the amount of radium present in my thorium nitrate solutions was determined.

I had at my disposal specimens of very different but known age, placed at my disposal by the firm Dr. O. Knöfler, of Berlin. As result I found that the specimens contained more radium the older they were, the oldest specimen of the year 1898 containing the most.

Then I obtained from the firm 100 grms. of quite freshly prepared thorium nitrate. The amount of radium in it was exceedingly small; the whole quantity of 100 grms. of the substance was used to measure it accurately. When referred to equal quantities of thorium the radium present in the new solution was scarcely 1/100 of that in the specimen nine years old.

It could not be assumed that the impurity of the older preparations was the cause of the greater amount of radium present, and it is just as improbable that thorium itself slowly decays to radium. Therefore I assumed that in the technical preparation of thorium another active substance was separated with it. This substance decays to radium, and is thus the long-sought direct mother substance of radium. In order to prove this, at the beginning of August I arranged the following experiments:—

1. One hundred grms. of thorium nitrate, obtained directly from the factory as perfectly fresh, were tested for radium in the way described above, after standing for four days. The result was calculated to the equivalent quantity. It was closed up on August 17th, and again tested on October 10th. The amount of radium was twice as large as before.

2. Forty grms. of thorium nitrate, prepared at the end of April, 1907, were also examined accurately for radium, allowed to stand over the holidays, and tested on October 11th. This amount also showed a considerable increase in the quantity of radium present.

3. Fifty grms. of thorium nitrate, prepared in June, 1907, were precipitated with oxalic acid from acid solution, the radium in the filtrate determined, and again it was allowed to stand over the holidays, and tested in October. In this case there was no increase in the amount of radium. Thus the mother substance is contained in the thorium precipitate. This was accidentally mixed with another preparation, and therefore was not examined further.

4. About 1 mgrm. of radio-thorium (activity about 100,000) was as carefully as possible freed from the small percentage of radium it contained by precipitating it three times with ammonia, and the remaining trace determined on August 15th. The specimen gave the same result on October 14th. The radio-thorium had been prepared from thorianite by precipitating with barium sulphate, and thus could not contain the mother substance of radium, which agrees with the above result.

In order to show the order of magnitude of the amount of radium found in some specimens, I append a few results. The quantity is referred to 100 grms. of thorium nitrate.

One hundred grms. of nitrate which had been obtained a few days before from the factory as only just prepared, contained about 3×10^{-11} grms. of radium bromide. The instruments I had did not allow me to determine the exact amount more accurately.

100 grms.	July, 1906,	contained	$5{\cdot}5 \times 10^{-10}$ grms.
„	Feb. 1902,	„	$2{\cdot}8 \times 10^{-9}$ „
„	„ 1900,	„	$4{\cdot}1 \times 10^{-9}$ „

The measurements were carried out with 10 grms. of the substance, except in the case of the perfectly new specimen.

Control experiments with other specimens of thorium are also being arranged.

If the amounts of uranium and thorium present in monazite sand are known, and if it is assumed that the total quantity of thorium and the total quantity of the mother substance of radium are obtained in the thorium preparation, it can be calculated how many grms. of radium are contained in a given amount of thorium nitrate if there is equilibrium between the radium and its parent substance in the thorium.

Now the quantities of uranium and thorium in different specimens of monazite sand, even in those from the same place, vary within certain limits. But it may safely be said that the average amount of uranium in Brazilian monazite sand is 0·3 per cent, and of thorium oxide, roughly, 5 per cent. The amount of thorium is frequently rather higher, but it must not be assumed that the thorium is quite quantitatively extracted in its preparation. Thus, 5 per cent is certainly the right order of magnitude. Now, 1 grm. of uranium in any uranium mineral contains, roughly, $0{\cdot}65 \times 10^{-6}$ grms. of radium bromide. By a simple calculation it may be found from the above assumption that 100 grms. of thorium nitrate + the mother substance of radium in equilibrium with radium must contain, roughly, 2×10^{-6} grms. of radium salt (calculated as bromide).

From this number, and the values obtained above by purely experimental methods for the amount of radium in different specimens of thorium of known age, according to the equation $I/I_\infty = 1 - e^{-\lambda t}$, the constant λ can be calculated, and from λ the decay period of radium. Hence, the values found for the decay period from the above results for three different thorium specimens are 3250 years, 2840 years, and 2630 years. As only a mean value is assumed for the amounts of uranium and thorium present, naturally variations in them cause corresponding variations in the decay period. Until more exact measurements are made the values can only be regarded as giving the order of magnitude of the decay period, and can lay no claim to great accuracy. The values found differ widely from a value recently determined by Cameron and Ramsay (*Journ. Chem. Soc.*, xci.,1266) for the decay constant of radium; for these investigators, from the volumes of the emanation developed from radium in a given time, deduced for the mean duration of life of radium 236 years, which gives 163 years for the decay constant. On the other hand, the numbers given above agree satisfactorily with the value 2600 years found by Rutherford. No explanation of the great difference in Rutherford and Ramsay's numbers is as yet forthcoming. Further researches with the newly discovered mother substance of radium will give an explanation of this important question.

Owing to the characteristic properties of "ionium" this new element can easily be completely separated from uranium minerals which contain little or no thorium; with my thorium preparations from monazite sand, which is so poor in uranium, or from monazite itself, it was not possible to get a pure product, as a method of separation from thorium is not yet known.

The part of pitchblende which follows the reactions of thorium will provide the cheapest material for the more thorough investigation of the new substance.

I beg to offer my best thanks to the Jager Foundation, of Berlin, for furnishing me with means for the above research.—*Berichte*, xl., 4415.

A NEW CONSTANT FOR BUTTER ANALYSIS.

By T. R. HODGSON, B.A., A.I.C.

THE analysis of butter is a constant source of trouble to the public analyst, partly because the present constants are variable for different samples and partly because the constants of the most common adulterants approach so closely to those of butter that it is possible to add to a very good sample of butter comparatively large quantities of the adulterant before the constants are brought down to the lowest value which is consistent with pure butter.

Another circumstance which makes the carrying out of the law with regard to pure butter almost an impossibility is that the adulteration is now carried on scientifically, and the unscrupulous man is able to add large quantities of other fats and oils to a good sample and smaller quantities to inferior samples, knowing full well that the resulting mixture will pass all the tests at the command of the analyst.

The author hopes that the constant described in this paper may go some way towards a mitigation of this evil.

The constant depends upon the oxidation with potassium permanganate of the acids obtained from butter fat after saponification with caustic potash and acidification with sulphuric acid. The author has found that the quantity of oxygen required to oxidise a given quantity of the saponified fat is, in the case of butter fat, invariable.

The method used is as follows:—The sample of butter is melted in a water-oven, and filtered through a dry filter-paper; 1 grm. of the filtered fat is then weighed out into a flask, and 25 cc. of a half normal alcoholic solution of caustic potash are added; the flask is then attached to a reflux condenser, and the whole is heated on a boiling water-bath for thirty minutes.

After the saponification the flask is detached from the condenser, and the solution is evaporated to dryness on a boiling water-bath; 50 cc. of distilled water are then added to the residue, and the whole again evaporated to dryness; this operation being continued until the whole of the alcohol is driven off. After the whole of the alcohol has been driven off, the residue is dissolved in water, and made up to 1000 cc.; 20 cc. of this solution are measured out into a beaker, and 50 cc. of a tenth-normal solution of potassium permanganate added and 50 cc. of a roughly 50 per cent solution of sulphuric acid; the beaker is then placed on a boiling water-bath for half-an-hour, and the excess of potassium permanganate is titrated back with a tenth-normal solution of oxalic acid, or with a standard solution of ferrous ammonium sulphate, preferably the latter.

Twenty-one samples of butter were examined, nineteen of which were of known purity, and were obtained in and around Birmingham, and two contained a proportion of margarine.

Sample.	$K_2Mn_2O_8$ used. Cc.	Sample.	$K_2Mn_2O_8$ used. Cc.
A.	41·8	M.	41·8
B.	41·8	N.	41·8
C.	41·8	O.	41·8
D.	41·8	P.	41·8
E.	41·8	Q.	41·8
F.	41·9	R.	41·8
G.	41·8	S.	41·8
H.	41·9	T.	30·0
I.	41·9	X.	36·2
K.	41·8	Z.	41·8
L.	41·8		

The Samples T and X were more or less mixed with margarine. As will be seen from the above figures the number of cc. of the permanganate solution used remains practically constant throughout.

From the number of cc. of permanganate solution used, the number of grms. of oxygen absorbed in the oxidation

of 1 grm. of the butter fat can be calculated, and this number multiplied by 100 gives what, for want of a better name, I propose to call the "oxygen equivalent."

This number, in the case of pure butter fat, is practically invariable, and is 167·2.

An attempt was first made to obtain the constant by direct titration with the permanganate solution, but the only result was a copious black precipitate of oxide of manganese and no apparent end-point.

The influence of time on the oxidation is not very marked; the oxidation was carried out as before, with the exception that the time of heating on the water-bath varied from five minutes to one hour; the variation in the number of cc. of permanganate solution used was 37·2 at the end of five minutes to 41·8 at the end of one hour; with consequent variation in the "oxygen equivalent" from 148·8 to 167·2; at the end of thirty minutes the oxidation ceases, and, apparently, no oxidation occurs between that time and one hour.

Time. Minutes.	$K_2Mn_2O_8$ used. Cc.	Oxygen equivalent.
5	37·2	148·8
10	37·6	150·4
15	37·9	151·6
20	38·2	152·8
25	40·0	160·0
30	41·8	167·2
35	41·8	167·2
40	41·8	167·2
45	41·8	167·2
50	41·8	167·2
55	41·8	167·2
60	41·8	167·2

It was the intention of the author in undertaking this piece of work to devise a method by which it would be possible to detect the presence of cocoanut oil in butter, and he hopes that the results given in this and two following papers may at least lead to such a method.

Analytical Department,
University of Birmingham.

A NECESSARY MODIFICATION OF VOLHARD'S METHOD FOR THE DETERMINATION OF CHLORIDES.*

By M. A. ROSANOFF and ARTHUR. E. HILL.

(Concluded from p. 265).

2. *On the Determination of Bromides and Iodides.*

We now turn to the determination of bromides. A solution made up of 200 cc. of water, 2 cc. of a saturated solution of iron-alum, and 1 drop of a solution of NH_4CNS, was thrown upon 0·5 grm. silver bromide in a stoppered bottle, and the mass vigorously shaken. After ten seconds no change of colour was noticeable; after thirty seconds the colour had become but slightly less intense. It seemed probable, therefore, that in ordinary titrimetric work the end-point would not be affected by the presence of solid bromide. This is, in fact, shown by the following four results, of which Nos. 1 and 2 were obtained by titration in presence of the bromide, Nos. 3 and 4 with the bromide filtered out.

1. .. .. 5·366 grms. Br per litre
2. .. .. 5·366 ,,
3. .. .. 5·357 ,,
4. .. .. 5·359 ,,

The slight disparity of the results obviously lies within the limits of experimental error.

With reference to the determination of iodides, we have been unable to observe any diminution in the intensity of iron sulphocyanate coloration even after the coloured solution had been shaken with silver iodide for one-half hour.

It is thus clear that in the determination of bromides and iodides it is unnecessary to filter out the silver precipitate before titrating with sulphocyanate.

3. *The End-point.*

The reactions between dissolved sulphocyanates and solid silver halides are, like all similar reactions, reversible.

For instance, $AgCl + \bar{C}NS \rightleftarrows AgCNS + \bar{C}l$. The transformation of sulphocyanates by silver chloride has been discussed above. The opposite reaction may be readily demonstrated by shaking silver sulphocyanate with an ammonium chloride solution containing some iron-ammonium alum: dissolved sulphocyanate shows up in a very short time.

In equilibrium,—

$$C^+_{Ag} \cdot C^-_{Cl} = S^2_{AgCl} \text{ and } C^+_{Ag} \cdot C^-_{CNS} = S^2_{AgCNS};$$

where C stands for concentration and S for solubility in pure water (both in molecules per litre). By division,—

$$\frac{C^-_{Cl}}{C^-_{CNS}} = \frac{S^2_{AgCl}}{S^2_{AgCNS}}.$$

Taking Böttger's recently solubility figures (*Zeit. Phys. Chem*, 1903, xlvi., 602), $S_{AgCl} = 1{\cdot}06 \cdot 10^{-5}$ and $S_{AgCNS} = 8{\cdot}27 \cdot 10^{-7}$. Hence,—

$$\frac{C^-_{Cl}}{C^-_{CNS}} = \frac{1{\cdot}12 \cdot 10^{-10}}{6{\cdot}84 \cdot 10^{-13}} = \text{about } 164.$$

Since similar salts are dissociated to the same degree, the ratio of the total (dissociated and undissociated) amounts of chloride and sulphocyanate in equilibrium with AgCl and AgCNS is also about 164. (The general theory of such equilibria in salt solutions was first given by Nernst in his "Theoretische Chemie," Ed. 1, Stuttgart, 1893, p. 426; Ed. 3, Stuttgart, 1900, p. 498). When, therefore, the ammonium sulphocyanate contained in a drop of solution is brought into contact with silver chloride, 164/165 of it are transformed into chloride and only 1/165 remains sulphocyanate. In other words, to produce the permanent colour-effect that a single drop of NH_4CNS would have in the absence of AgCl, no less than 165 drops of NH_4CNS are required when AgCl is present. Such intensity of colour is, however, unnecessary. We find that the eye can detect the coloration due to about 1/15 of a drop of N/10 NH_4CNS in 200 cc. of water containing 5 cc. saturated iron-alum solution. To establish such a coloration permanently in the presence of AgCl, $165 \div 15 = 11$ drops of sulphocyanate solution are required. If the amount of silver nitrate required to precipitate the chloride in a given solution is about 25 cc., the error committed in a perfect sulphocyanate titration in the presence of the silver chloride would amount to about 2 per cent. Ordinarily it will be smaller; the smaller the less diligently one stirs the solution.

It might be similarly shown that in the case of bromides and iodides the interference of the precipitates with the end-point is negligible (see Note). Dynamic theory is thus throughout in agreement with the verdict of our experiments.

Note.—Taking Böttger's figures (*loc. cit.*) for the solubilities of AgBr and AgCNS and Kohlrausch and Dolezalek's figure (*Ber. Berlin Akad.*, 1901, p. 101) for

* Presented before the New York Section of the American Chemical Society, December 7, 1906. From the *Journal of the American Chemical Society*, xxxix., No. 3.

the solubility of AgI, the ratios of the solubility products involved are as follows :—

$$\frac{S^2_{AgBr}}{S^2_{AgCNS}} = \frac{C^-_{Br}}{C^-_{CNS}} = \frac{2{\cdot}03 \cdot 10^{-13}}{6{\cdot}84 \cdot 10^{-13}} = \text{about } 0{\cdot}3$$

(that is, of a drop of sulphocyanate added, three-thirteenths will be changed to bromide, but ten-thirteenths will remain unchanged) ;

$$\frac{S^2_{AgI}}{S^2_{AgCNS}} = \frac{C^-_{I}}{C^-_{CNS}} = \frac{2{\cdot}25 \cdot 10^{-16}}{6{\cdot}84 \cdot 10^{-13}} = \text{about } 0{\cdot}00033$$

(that is, of a drop of sulphocyanate added, only about 1/3000 will be changed to iodide).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 7th, 1907.

Sir WILLIAM RAMSAY, K.C.B., F.R.S., President, in the Chair.

MESSRS. P. C. Austin, C. Hollins, and L. G. Killby were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Edward de Barry Barnett, 40, Queensborough Terrace, Hyde Park, W. ; Frederic William Caton, B.A., B.Sc., 6, King Street, Snow Hill, E.C. ; George Hugh Crisp, B.A., 62, Gainsboro' Road, Crewe ; Claude Scott Fawcitt, Darlington, England ; and Shimoga S.M.Ry., India.

Of the following papers, those marked * were read :—

*207. "*Gaseous Nitrogen Trioxide.*" By HERBERT BRERETON BAKER and MURIEL BAKER.

The authors have found that liquid nitrogen trioxide can be converted into the gaseous state if it is dried completely. Seventeen determinations of the density of the gas have been made by Victor Meyer's method in very dry nitrogen. Several different preparations were used and the densities varied from 38 to 62. The density corresponding to the formula N_2O_3 is 38, and it is concluded that there is partial polymerisation to the double molecule N_4O_6. The analysis of the substance gave 63·12 per cent of oxygen (mean of five experiments), the calculated value for the trioxide being 63·09. Determinations of the molecular weight by the cryoscopic method in dried benzene gave 83 and 83·2 for one sample and 95 for another. The liquid is green at the ordinary temperature, but becomes blue below −2°. It does not solidify at −80°, but in liquid air it solidifies to a mass of very dark blue crystals.

DISCUSSION.

Dr. VELEY asked if the authors had examined the effect of sunlight on nitrogen trioxide, as it appeared possible that the variations in composition and density of the several samples examined might be due to this cause.

The observation of the authors that nitrogen trioxide does not dissolve in water to form nitrous acid, as such, seemed of especial interest ; although this acid was frequently represented as a reagent in chemical change, yet those who had worked on the subject had begun to realise that nitrous acid was possibly no better than a convenient fiction.

Dr. DIVERS called attention to the fact that, two years ago, Raschig (*Zeit. Angew. Chem.*, 1905, xviii., 1281), and Rây and Gañguli (*Proc.*, 1905, xxi., 280) showed, independently, that nitric oxide distinctly forms nitrogen trioxide with oxygen before it goes on to produce nitric peroxide, and thus furnished chemical evidence, for the first time, of the existence of nitrous anhydride, N_2O_3, in the gaseous state.

Dr. BAKER, in reply, stated that sunlight had not been observed to exert any effect on nitrogen trioxide.

*208. "*The Atomic Weight of Tellurium.*" By HERBERT BRERETON BAKER and ALEXANDER HUTCHEON BENNETT.

The investigation of tellurium and the possibility of its containing another element has been the subject of study for the last thirteen years. The following methods were used in attempting to split up the element :—(1) Fractional crystallisation of telluric acid prepared by two distinct processes. (2) Solution of barium tellurate in water. (3) Fractional distillation of (*a*) tellurium, (*b*) tellurium tetrachloride, and (*c*) tellurium dioxide. (4) Conversion of tellurium into the hydride. (5) Fractional electrolysis of tellurium tetrachloride and tetrabromide. (6) Fractional precipitation of tellurium tetrachloride by water.

In none of these processes was any difference found in the various fractions. Two methods were described for finding the equivalent of the element. The first, which depends on the reduction of the dioxide to the element by means of sulphur, gave 127·60 as the atomic weight (mean of twenty-five determinations), and the second, depending on the conversion of the element into the tetrabromide, gave 127·61 (mean of eighteen determinations).

DISCUSSION.

The PRESIDENT remarked that no research is final, but this one must go a long way to settle the question of the homogeneity of tellurium.

Dr. Percy Williams, many years ago, carried out at University College some experiments on the subject. Tellurium, purified by crystallisation of its double bromide with potassium, gave, on reducing its oxide with hydrogen and absorbing volatilised metal with silver foil, the number 127·6 for the atomic weight. The double bromide, owing to the crystals retaining mother-liquor, was not adapted for an atomic weight determination.

*209. "*The Isomerism of the Double Sulphites of Sodium and Potassium.*" By MICHAEL HARRY GODBY.

By neutralising potassium hydrogen sulphite with sodium hydroxide and sodium hydrogen sulphite with potassium hydroxide, two solutions are produced from which opaque, greasy crystals are obtained with some difficulty. They are of somewhat variable composition as regards water of crystallisation, and contain the metals in unequal atomic proportions, generally about 60 atoms of sodium to 40 of potassium.

These crystals, when heated with ethyl iodide to 130—140° in a sealed tube, yield a salt which can be crystallised from boiling alcohol and contains ethyl, sodium, potassium, iodine, and SO_3. In each case, there are present about 76 atoms of potassium for every 24 of sodium.

An attempt was made to prepare the double sulphites from the two solutions by precipitating with alcohol, as recommended by Röhrig. Fine powdery, white crystals were obtained having almost exactly the composition required for $KNaSO_3$.

These crystals, when heated with ethyl iodide as before and the product extracted with boiling alcohol, gave a white, finely-crystalline salt, which was re-crystallised from boiling alcohol. This salt, whether obtained from the solution made originally by neutralising potassium hydrogen sulphite with sodium hydroxide or by neutralising sodium hydrogen sulphite with potassium hydroxide, contained sodium, potassium, ethyl, SO_3, and iodine in the same proportions, and approximated fairly closely to the salt prepared by Schwicker (*Ber.*, 1889, xxii., 1728) to which he ascribes the formula $4(KEtSO_3)NaI$, but contained 28 atoms of sodium to 72 of potassium, instead of 20 to 80 respectively.

There is no evidence for the existence of two isomeric salts, $KO{\cdot}SO_2Na$ and $NaO{\cdot}SO_2K$.

*210. "*Studies in the Camphane Series.* Part XXIV. *Camphoryldithiocarbamic Acid and Camphorylthiocarbimide.*" By MARTIN ONSLOW FORSTER and THOMAS JACKSON.

Camphoryldithiocarbamic acid, $C_8H_{14}\begin{cases}CH\cdot NH\cdot CS\cdot SH\\ |\\ CO\end{cases}$,

prepared from aminocamphor and carbon disulphide, is much more stable than compounds of this class which have been hitherto described, and does not decompose below its melting point, 128°. The *methyl* ester, $C_{12}H_{19}ONS_2$, melts at 147°, and is resolved into camphorylthiocarbimide and methyl mercaptan at 170°; the *benzoyl* derivative, $C_{18}H_{21}O_2NS_2$, crystallises from petroleum in colourless, silky needles melting at 105°. Nitrous acid oxidises the dithiocarbamic acid to the thiocarbimide and sulphur, but if amyl nitrite is added to an ethereal solution of the acid an intermediate *compound*, $C_{11}H_{15}ONS_2$, is produced, which melts at 110°, and breaks up readily into sulphur and the mustard oil.

Camphorylthiocarbimide, $C_8H_{14}\begin{cases}CH\cdot N:C:S\\ |\\ CO\end{cases}$, obtainable

in a variety of ways from the dithiocarbamic acid, melts at 106·5°, and combines readily with bases, but less freely with alcohols; *camphorylthiocarbamide*, $C_{11}H_{18}ON_2S$, arising from it by the action of dry ammonia, melts at 180°, and *dicamphorylthiocarbamide*, $C_{21}H_{32}O_2N_2S$, obtained by prolonged treatment with water, melts at 176°. *Camphorylphenylthiosemicarbazide*, $C_{17}H_{23}ON_3S$, occurs in two modifications, melting at 183° and 163° respectively; these are distinguishable by a variety of colour reactions, and by the readiness with which the less fusible form passes into the *anhydride*, $C_{17}H_{21}N_3S$, which melts at 235°.

DISCUSSION.

Mr. W. C. REYNOLDS observed that supersaturated solutions of the alkaloid hyoscyamine in some solvents, such as water and wet ether, behaved in a similar manner to the case described by Dr. Forster.

Mr. A. C. CHAPMAN remarked that the glucoside apiin was another substance in which a remarkable relationship existed between the jelly and the crystalline forms.

The PRESIDENT suggested the analogy between the phenomena mentioned by Dr. Forster and other gentlemen and superfusion. Alcohol, when cooled, solidifies to a glass; on standing for a couple of days, crystallisation sets in, as indeed it does in the long run with ordinary glass. In the instances adduced by Dr. Forster, no doubt surface tension phenomena are concerned.

*211. "*The Vapour Pressures of Triethylamine, of 2:4:6-Trimethylpyridine, and of their Mixtures with Water.*" By ROBERT TABOR LATTEY.

A study of the total pressure curves for these mixtures shows that they conform to the type predicted by theory. The partial pressure curves can be calculated by a form of the Duhem-Margules equation. In both cases the curves show a maximum where the compositions of vapour and liquid are identical. At temperatures where the miscibilities of the components are limited there are indications of a second maximum inside the "unreal" parts of the curves.

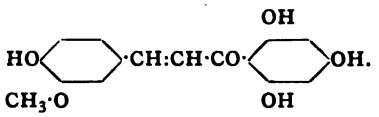
*212. "*Liquid Triethylamine.*" By ROBERT TABOR LATTEY.

A comparison of the vapour pressures and critical constants of triethylamine and other liquids leads to the belief that the amine is a unimolecular liquid. This is confirmed by a determination of the temperature-coefficient of the molecular surface energy.

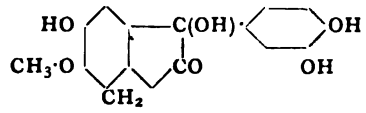
*213. "*Note on the Constitution of Homoeriodictyol.*" By FREDERICK BELDING POWER and FRANK TUTIN.

At the meeting of the American Pharmaceutical Association held in September, 1906, a paper was communicated by the authors entitled "Chemical Examination of Eriodictyon" (*Proc. Amer. Pharm. Assoc.*, 1906, liv., 352; Abstr., 1906, ii., 885). In this communication, we described the isolation and properties of three new crystalline substances, one of which possessed the formula $C_{16}H_{14}O_6$, and was designated homoeriodictyol. Early in the following year, G. Mossler (*Annalen*, 1907, cccli., 233) described the results of an examination of the same drug. Mossler had also isolated from *Eriodictyon* leaves the substance possessing the formula $C_{16}H_{14}O_6$, but proposed to name it "eriodictyonon."

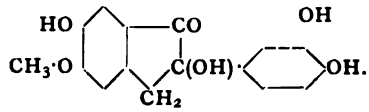
At the time of the appearance of the latter paper, we were engaged in further work on homoeriodictyol, the results of which (*Trans.*, 1907, cxi., 889) led us to assign to this substance the following constitutional formula—



We have recently been favoured by Dr. Mossler with a reprint of a paper communicated by him to the Academy of Sciences in Vienna (*Sitzungsber. K. Akad. Wiss. Wien.*, June, 1907, [2], cxvi.) at a time when he was unaware of our second investigation. In this most recent paper he sets forth the conclusion that homoeriodictyol ("eriodictyonon") is represented by one of the following formulæ :—



or—



It is stated by Mossler that the action of alkalis on homoeriodictyol results only in the formation of a red resin, but this is not the case, as it was shown in our second communication that the product of this action although highly coloured and containing a considerable amount of tarry matter, consists to a large extent of a mixture of ploroglucinol and ferulic acid. It follows from this that neither of the above formulæ proposed by Mossler can correctly represent the constitution of homoeriodictyol, as substances possessing such configurations could not possibly give rise to phloroglucinol. On the other hand, a ready explanation of the formation of all the substances obtained from homoeriodictyol by Mossler is afforded by assigning to this compound the constitution which we have proposed.

Although the observation, recorded by Mossler, that the action of bromine on homoeriodictyol is one of substitution, and not of addition, might be taken as evidence in support of the conclusion that the latter substance was saturated, it cannot be considered as proof that an ethylenic linking is not present.

The statement made by Mossler that homoeriodictyol possesses optical activity, is in direct conflict with our views regarding the constitution of this substance, as the formula we have proposed contains no asymmetric carbon atom. We had previously examined tetra-acetylhomoeriodictyol polarimetrically, but without being able to detect any optical activity, and have now repeated this experiment with the same result. Homoeriodictyol, also, has now been examined in this direction, and we can definitely state that our material is optically inactive. So far as we are aware, therefore, no facts have yet been recorded which are not in harmony with the formula we have assigned to homoeriodictyol.

214. "*The Alkyl Compounds of Gold. Diethylauric Bromide.*" (Preliminary Note). By WILLIAM JACKSON POPE and CHARLES STANLEY GIBSON.

Auric bromide reacts vigorously with magnesium ethyl bromide in ethereal solution, and from the product *diethylauric bromide*, $(C_2H_5)_2AuBr$, has been separated; this is the first alkyl gold compound to be described.

Diethylauric bromide dissolves in the ordinary organic solvents, but is insoluble in water. It crystallises in long colourless needles which melt at 58° with slight decomposition; on rapid heating, it decomposes explosively at about 70°. The compound has an odour resembling that of bromocamphor, and volatilises on warming in a vacuum. It is much more readily acted on by reagents than is the recently discovered trimethylplatinic iodide, $(CH_3)_3PtI$; thus the former yields crystalline products on treatment with ammonia and nitric acid, whilst the latter is unaffected by those reagents.

The study of the alkyl compounds of the metals of Groups I. and VIII. of the periodic classification is being continued.

215. "*The Interaction of Methylene Chloride and the Sodium Derivative of Ethyl Malonate.*" (A Correction). By FRANK TUTIN.

In a paper bearing the above title (*Trans.*, 1907, xci., 1141), three crystalline substances were described as by-products of the reaction which takes place when methylene chloride is heated with the sodium derivative of ethyl malonate. It has now been ascertained that one of these substances, described as "the yellow sodium salt," is the sodium derivative of "ethyl dicarboxyglutaconate," and had been formed from chloroform which was present as an impurity in the methylene chloride. The acid obtained by the hydrolysis of this sodium compound, and to which the formula $C_{10}H_{12}O_8$ was assigned, must therefore have been glutaconic acid, $C_5H_6O_4$.

216. "*Preparation of Aliphatic Nitro-compounds by the Interaction of the Alkyl Iodides and Mercurous Nitrite.*" By PRAFULLA CHANDRA RAY and PANCHANAN NEOGI.

By the interaction of mercurous nitrite and the alkyl iodides, namely, methyl, ethyl, *iso*propyl, and *iso*amyl iodides, the corresponding nitro-compounds and the esters are formed. In this respect, mercurous nitrite behaves exactly like silver nitrite. The yields obtained were as follows:—[(*a*) = with silver nitrite, (*b*) = with mercurous nitrite]. Methyl iodide (28 grms.) gave (*a*) methyl nitrite, 3·6 grms., and nitromethane, 4·0 grms., (*b*) 2·1 grms. and 2·6 grms. respectively. Ethyl iodide (60 grms.) gave (*a*) ethyl nitrite, 12·8 grms., and nitroethane, 12·1 grms., (*b*) 8·8 grms. and 9·2 grms. respectively. *iso*Propyl iodide (34 grms.) gave (*a*) *iso*propyl nitrite, 8·0 grms., and nitro-*iso*propane, 6·3 grms., (*b*) 4·1 grms. and 3·8 grms. respectively.

*iso*Amyl iodide (76 grms.) gave (*a*) *iso*amyl nitrite, 3·2 grms., and nitro*iso*pentane, 12·4 grms., (*b*) 3·2 grms. and 7·8 grms. respectively.

217. "*Some Mercury Derivatives of Camphor.*" By JAMES ERNEST MARSH and ROBERT DE JERSEY FLEMING STRUTHERS.

When camphor is heated with an alkaline solution of mercuric iodide, mercury derivatives of camphor are formed. By treatment with glacial acetic acid, *camphor dimercuri-iodide*, $C_{10}H_{14}O,Hg_2I_2$, is precipitated. The filtrate, when diluted with water, gives with potassium iodide, or, better, with a solution of mercuric iodide in potassium iodide, an orange precipitate of the double salt, $C_{10}H_{15}O,HgI + HgI_2$. This, on treatment with potassium iodide in neutral solution, gives *camphor mercuri-iodide*, $C_{10}H_{15}O,HgI$, which is pale yellow. The above-mentioned acetic acid solution also gives with potassium chloride and bromide white precipitates of *camphor mercuri-chloride*, $C_{10}H_{15}O,HgCl$, and *camphor mercuri-bromide*, $C_{10}H_{15}O,HgBr$, respectively, which, however, have not yet been obtained quite free from iodide.

218. "*Contributions to the Chemistry of the Terpenes.* Part II. *The Oxidation of Limonene with Chromyl Chloride.*" By GEORGE GERALD HENDERSON.

When a dilute solution of chromyl chloride in carbon disulphide is slowly added to a similar solution of limonene, an *additive product*, $C_{10}H_{16},2CrO_2Cl_2$, is precipitated. This compound is a brown powder, which begins to decompose in moist air, and at once reacts with water, yielding a solution of chromic chloride, some resinous matter, and a brown viscous liquid insoluble in water. When subjected to distillation in steam, the brown liquid yields a further quantity of resinous matter and a clear yellow oil, which is composed of an aldehyde, a ketone, and a very unstable substance containing chlorine as well as oxygen. The *aldehyde*, $C_{10}H_{14}O$, is a strongly odorous oily liquid, b. p. 221—222°/755 mm. It yields a crystalline *semicarbazone*, m. p. 156°. It is unsaturated, and on exposure to air it is converted into the corresponding *acid*, $C_{10}H_{14}O_2$, which forms small colourless crystals, m. p. 172°. The *silver* salt of the acid crystallises in small white prisms. Boiling dilute nitric acid converts the aldehyde slowly into *p*-toluic acid; this is also the chief product when the aldehyde is oxidised with a dilute solution of potassium permanganate. The *ketone*, $C_9H_{12}O$, is the chief constituent of the oxidation product. It is an almost colourless oily liquid with a strong odour, b. p. 112—113°/15 mm. It is unsaturated. The *semicarbazone* of the ketone crystallises with one molecule of methyl alcohol in colourless prisms which quickly effloresce in the air. After heating at 100°, it melts at 205°. When heated with ammonium formate in a sealed tube, the ketone is converted into the formyl derivative of an amine, from which the free *amine*, $C_9H_{13}{\cdot}NH_2$, is obtained by hydrolysis with alcoholic potash. It is a colourless oily liquid with a disagreeable odour and an alkaline reaction, and is almost insoluble in water. The hydrochloride and the sulphate of the amine are deliquescent, and very readily soluble in water or alcohol; the *platinichloride*, which is very sparingly soluble in water, crystallises in small brownish yellow needles. The chlorinated oxidation product is so unstable that it could not be isolated.

219. "*The Synthesis of Acridines and Phenonaphthacridines. Tetra- and Hexa-methylacridines, Dimethylphenonaphthacridines, Dixylylmethylenediamines.*" By ALFRED SENIER and ARTHUR COMPTON.

By the interaction of methylene dichloride and xylidines, with or without xylenols, two methylenediamines are formed which by means of Ullman's method of substitution (*Ber.*, 1903, xxxvi., 1019) gave rise to two corresponding acridines. One of the latter can also be obtained by heating the methylenediamine to a higher temperature, whereas the other cannot. This is explained by assuming that, when the *p*-position with respect to the amino-group in the arylamine is not substituted, the methylenediamine first formed is changed by metastasis to a methylenebenzidine (*pp*-diaminodiarylmethane) from which no acridine can result.

When, however, the *p*-position is occupied by an alkyl group, the metastatic action produces an *oo*-diaminodiarylmethane from which an acridine is easily derived. By the interaction of methylene dichloride and mixtures of xylidines and naphthols, corresponding dimethylphenonaphthacridines are obtained.

The following compounds were described:—*Di*-1 : 3 : 4-*xylylmethylenediamine* (compare Senier and Goodwin, *Trans.*, 1902, lxxxi., 284). 1 : 3 : 7 : 9-*Tetramethylacridine*; its *platinichloride*, *aurichloride*, and *picrate*. *Di*-1 : 4 : 5-*xylylmethylenediamine* and its *platinichloride*. 1 : 4 : 6 : 9-*Tetramethylacridine* and its *aurichloride*. 1 : 3 : 4 : 6 : 7 : 9-*Hexamethylacridine* (compare Senier and Goodwin, *loc. cit.*).

Di-ψ-*cumylmethylenediamine*. 9 : 11-*Dimethylpheno*-N-α-CH_3-*naphthacridine* and its *platinichloride*. 9 : 11-*Dimethyl*-

pheno-$\begin{matrix}\text{N-}\beta\\|\\\text{CH}\alpha\end{matrix}$*-naphthacridine* (compare Ullmann, *Chem. Centr.*, 1901, ii., 568). 8 : 11-*Dimethylpheno-*$\begin{matrix}\text{N-}\alpha\\|\\\text{CH}\beta\end{matrix}$*-naphthacridine* and its *platinichloride*. 8 : 11-*Dimethylpheno-*$\begin{matrix}\text{N-}\beta\\|\\\text{CH}\alpha\end{matrix}$*-naphthacridine* and its *platinichloride*.

220. "*Chemical Examination of the Root and Leaves of Morinda longiflora.*" By MARMADUKE BARROWCLIFF and FRANK TUTIN.

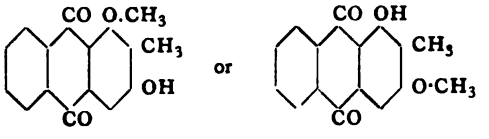
The root and leaves of *Morinda longiflora*, G. Don, a West African plant known as "Ojuologbo," and stated to possess valuable medicinal properties (*Journ. Soc. Arts*, 1905, liii., 1069), have been chemically examined.

The ground materials were extracted with hot alcohol, and the resulting extracts separately investigated. No alkaloid was present in either material.

The extract yielded by the root gave a small quantity of a *hydroxymethoxymethylanthraquinone*, $C_{16}H_{12}O_4$ (m. p. 290°), and a small amount of a monoethyl ether of alizarin. It also yielded, in addition to resins and other amorphous products, formic, acetic, butyric, palmitic, and citric acids, a phytosterol, $C_{27}H_{46}O$ (m. p. 130°), and a large amount of a sugar which gave *d*-phenylglucosazone (m. p. 215°).

The extract of "Ojuologbo" leaves gave, in addition to some of the substances mentioned above, a small amount of the hydrocarbon hentriacontane, and a new crystalline *alcohol*, $C_{38}H_{61}O_3{\cdot}OH$ (m. p. 278°; $[\alpha]_D$ +65·9°), designated *morindanol*. This compound, on treatment with sodium ethoxide and methyl iodide, yields *methylmorindanol*, $C_{38}H_{61}O_3{\cdot}OCH_3$ (m. p. 116°).

The above-mentioned hydroxymethoxymethyl-anthraquinone yields, on methylation, 1 : 3-*dimethoxy-2-methylanthraquinone* (m. p. 181°), and, on heating with 70 per cent. sulphuric acid, it gives 1 : 3-dihydroxy-2-methylanthraquinone. It must therefore be represented by one of the following formulæ :—



On heating with hydriodic acid, it yields a *dihydroxymethylanthranol*, $C_{15}H_{12}O_3$ (m. p. 235°).

The monomethyl ether of alizarin is identical with the compound of this nature which was isolated by Perkin and Hummel (*Trans.*, 1893, lxiii., 1174) from "Chay root."

Neither of the extracts possessed any pronounced physiological activity.

221. "*Ethyl α-cyano-γ-phenylacetoacetate.*" By ARTHUR RICHARD SMITH and JOCELYN FIELD THORPE.

Contrary to the observation of Haller, it is found that ethyl *α*-cyano-*γ*-phenylacetoacetate, $CH_2Ph{\cdot}CO{\cdot}CH(CN)CO_2Et$, is a well-defined, crystalline substance, which melts at 25°, and distils without decomposition at 178° (20 mm.). The compound is a strong acid, readily decomposing carbonates, and yielding salts which can be recrystallised from water without undergoing dissociation. The alkali salts are not acted on by alkyl iodides, but if the silver salt is treated, in dry ether solution with ethyl iodide a mixture of *ethyl α-cyano-γ-phenyl-α-ethylacetoacetate*, $CH_2Ph{\cdot}CO{\cdot}CEt(CN)CO_2Et$, and *ethyl α-cyano-β-ethoxy-γ-phenylcrotonate*, $CH_2Ph{\cdot}C(OEt){:}C(CN)CO_2Et$, is produced. The former is a liquid boiling at 190—191° (20 mm.), and the latter a solid melting at 66°. Characteristic derivatives of ethyl α-cyano-γ-phenylacetoacetate and of the two forms of its ethyl derivative were described.

222. "*Aromatic Amides and Imides of Camphoric Acid.*" By WILLIAM ORD WOOTTON.

The substance obtained by the action of nitrous acid on camphorylphenylhydrazide is found to be N-*nitroso-camphorylphenylhydrazide*, $C_8H_{14}{<}^{CO}_{CO}{>}N{\cdot}N(NO){\cdot}C_6H_5$, m. p. 157°, and not a nitro-compound as stated by E. M. Chaplin (*Ber.*, 1892, xxv., 2565). N-*Nitrocamphoryl-phenylhydrazide*, $C_8H_{14}{<}^{CO}_{CO}{>}N{\cdot}N(NO_2){\cdot}C_6H_5$, may be prepared by the action of nitric acid and acetic anhydride on camphorylphenylhydrazide, and forms colourless prisms melting and decomposing at 115—116°.

Camphoryl-4-bromophenylhydrazide,—

$$C_8H_{14}{<}^{CO}_{CO}{>}N{\cdot}NH{\cdot}C_6H_4Br,$$

and *camphoryldibromophenylhydrazide* have been prepared, together with their N-*nitroso*- and N-*nitro*-derivatives. It is found in each case that the nitroso-derivatives are pale yellow, whilst the nitro-compounds are colourless. The fact that the latter are readily reduced with elimination of ammonia indicates that the nitro-group is not attached to the benzene nucleus.

Camphoric anhydride combines with *p*-bromoaniline at 120° to form 4-*bromophenyl-α-camphoramic acid*, $CO_2H{\cdot}C_8H_{14}{\cdot}CO{\cdot}NH{\cdot}C_6H_4Br$, m. p. 207°. Reduction of the *nitro*-derivative of this acid yields 4-*bromo-3-aminophenyl-α-camphoramic acid*, m. p. 207.° 4-*Bromo-3-aminophenylcamphorimide*, $C_8H_{14}{<}^{CO}_{CO}{>}N{\cdot}C_6H_3Br{\cdot}NH_2$, has also been obtained. These two amino-compounds are optically active, and it is the author's intention to utilise them and certain of their derivatives in the study of racemic aldehydes.

Camphoric anhydride and aminoazobenzene combine to form 4-*benzeneazophenyl-α-camphoramic acid*, $CO_2H{\cdot}C_8H_{14}{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_5$, m. p. 223—224°. On reduction, 4-*aminophenyl-α-camphoramic acid* is obtained.

223. "*The Melting-point of* d-*phenylglucosazone.*" By FRANK TUTIN.

During the past few years a number of plants have been submitted to exhaustive investigation in the Wellcome Chemical Research Laboratories, and in all cases where sugar was found to be present the osazones were prepared. In a number of instances the phenylosazone obtained melted at a temperature considerably higher than that at which *d*-phenylglucosazone is stated to fuse, namely 205.° Several of these preparations melted at or above 215°, whilst the osazone yielded by the sugar contained in the leaves of *Gymnema silvestre* (Power and Tutin, *Pharm. Journ.*, 1904, lxxiii., 234) fused at 218—219°. Analyses of these preparations of high melting-point showed that they were the osazones of hexoses, and as the only compound of this class stated to melt above 206° is *a*-acrosazone (m. p. 217°), it was at first thought that they must be identical with this compound and were derived from inactive sugars.

It was, therefore, deemed of importance to recrystallise and examine a number of the specimens of osazones which had been prepared from plant sugars by different workers in these laboratories. With this end in view experiments were instituted with the object of finding a better means of purifying osazones than by re-crystallisation from alcohol, and it was ascertained that the use of pyridine was attended with excellent results. The osazone was dissolved in a small quantity of boiling pyridine, hot alcohol and subsequently a little water added, when, on allowing the mixture to cool, the osazone separated in a pure condition.

Specimens of osazones prepared from plant sugars were then recrystallised in this manner, with the results shown in the accompanying tables.

Source of sugar.	Original melting-point of osazone.	Melting-point after re-crystallisation.
Brucea antidysenterica (fruit) ..	205°	217°
,, ,, (leaves) .	205	215—216
Gymnema sylvestre (leaves) ..	218—219	217
Aethusa cynapium (herb)	218	217
Grindelia camporum (herb) ..	205—206	216
Chailletia toxicaria (fruit)	211—212	216
Eriodictyon Californicum (leaves)	205	216—217
Morinda longiflora (root)	215	216
Lippia scaberrima (herb)	210	216—217
Ipomoea purga (tuber)	217—218	217—218
Olea Europaea (bark)	216	217
Micromeria Chamissonis (herb) .	205	217

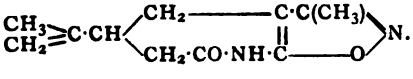
A specimen of *d*-phenylglucosazone (from dextrose) melting at 205° was then recrystallised in a similar manner, after which it melted at 217°. Furthermore, it was found that *d*-phenylglucosazone, when prepared from dextrose by the aid of freshly distilled phenylhydrazine, and avoiding a too protracted period of heating, exhibited an initial melting-point of 216°.

It is evident, therefore, that *d*-phenylglucosazone, when pure, melts at about 217°, and not at 205° as stated by Fischer (*Ber.*, 1884, xvii., 579).

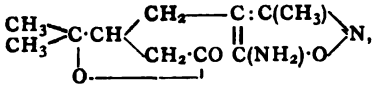
On referring to the original papers on the subject it will be found that α-acrosazone was originally obtained melting at 205° (Fischer and Tafel, *Ber.*, 1887, xx., 1093), and that it was only after careful purification that it exhibited a melting-point of 217° (*Ibid.*, p. 3389). It is evidently owing to the fact that *d*-phenylglucosazone was not submitted to an equally elaborate process of purification (*loc. cit.*) that the correct melting-point of this substance was not initially observed.

224. "*The Interaction of Cyanodihydrocarvone, Amyl Nitrite, and Sodium Ethoxide.* Part II. *The Constitution of the Products.*" By ARTHUR LAPWORTH and ELKAN WECHSLER.

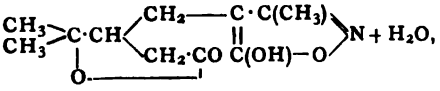
The compound obtained as the product in rhe above reaction and referred to in the first paper (*Trans.*, 1907, xci., 978) as "the lactam" (L), has the constitution—



The derived amino-acid (A), when acted on by acids, is converted into the "lactonic base" (B),—

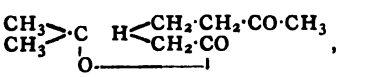


and the "lactonic acid,"—



successively.

On reduction with ferrous hydroxide in alkaline solution, the latter yields pure *d*-homoterpenoyl methyl ketone,—



ammonia, and carbonate.

The isomeric "lactonic base" (B'), erroneously assigned $[\alpha]_D$ 6·21, is quite inactive, and on reduction yields inactive homoterpenoyl methyl ketone. This base is therefore a racemic form of B. The isomeric lactam (L') is strongly active, but also yields the inactive keto-lactone on reduction.

PHYSICAL SOCIETY.

Ordinary Meeting, November 22nd, 1907.

Prof. J. PERRY, F.R.S., President, in the Chair.

MR. S. SKINNER exhibited specimens of Singing Sand from New England.

The specimens shown were from two sea-beaches in New England, one at Manchester, Mass., and the other near Small Point, Maine. The beaches are alike in character in being surrounded by hard rock walls and in not having streams which might bring silt flowing through them. The sands are consequently very clean and free from small particles; and this especially so after each tidal washing. The sand consists chiefly of angular clear quartz fragments. Mr. Skinner has been able to verify most of the facts observed by Mr. Carus Wilson (*Nature*, 1891), viz.:—1. The sounds are best obtained by plunging a hard plunger into a glazed cup containing the sand. 2. After a time the production of the sounds becomes difficult. 3. The sounding may be restored by washing, which presumably removes fine powder formed by attrition between the particles. 4. It is necessary that the displacement of the sand by the plunger should occur easily. If there is resistance due to the shape of the vessel, or due to clogging by dust, the sounding is stopped. The theory put forward in "Sound" by Professors Poynting and Thomson seems a reasonable explanation. They consider that Osborne Reynolds's discovery that there is an arrangement of minimum volume of a number of equal spheres in contact may afford a key to the phenomenon. "We may suppose the sand to consist of equal spheres, arranged when undisturbed so as to occupy minimum volume. When disturbed the mass may pass through many successive minima of volume before coming to rest."

Mr. L. BAIRSTOW exhibited a Micromanometer

The instrument exhibited was one of two which are in regular use at the National Physical Laboratory for measurements of pressures due to air currents. It was designed by Prof. Chattock and Mr. Fry for Dr. Stanton's work on "Air Pressures on Plane Surfaces," and is described in the *Proc. Inst. C. E.*, clvi., Part 2. An earlier description of a somewhat similar tilting-gauge was also given by Prof. Chattock in 1901 (*Phil. Mag.*, Jan., 1901). When the pressures on the two sides of the gauge are balanced the whole of the liquids employed are in their zero positions, and errors due to capillarity and viscosity are avoided. The gauge exhibited has a sensitiveness of 1/10,000 of an inch of water and a range of three-quarters of an inch of water. The gauge is slightly sensitive to temperature due to the expansion of the castor-oil used, but the changes are small and easily allowed for by taking time-readings of the zero. The gauge is not suitable for rapidly varying pressures, as considerable distortions of the oil-surface leads to an irregularly displaced zero.

Mr. A. CAMPBELL drew attention to the question of capillarity, and asked if the working of the instrument was affected by changes in the surface-tension and angle of contact of the liquids in the gauge.

Prof. H. A. WILSON suggested the use of liquids without appreciable vapour pressure.

Mr. BAIRSTOW, in reply, thought that the effects of surface-tension would not interfere with the correct working of the instrument.

A Diabolo Experiment was shown by Mr. C. V. BOYS.

Mr. Boys exhibited a diabolo spool which has the peculiar merit that no one can spin it. It is based upon the following principle:—Either the ordinary spool of commerce, which has its moment of inertia about its axis of rotational symmetry a minimum, or a spool not generally made which has the corresponding moment of inertia a maximum, has stable rotation about this axis or about a transverse axis, *i.e.*, if it is temporarily rotating about an axis inclined to one or other, it will tend to shift its

momentary axis of rotation, and gradually settle down so as to spin about one or other. If, however, the spool is so proportioned that the moment of inertia is identical about any axis, it has no tendency to spin stably about any particular axis, and the axis of rotation wanders about so rapidly that it cannot be spun. A heavy conical sheet projecting equally on either side of the vertex, whose semivertical angle is equal to $\tan^{-1}\sqrt{2}$, has this property; but such an ideal construction is impracticable. All added matter beyond the sheet in the direction of the axis makes the momental ellipsoid more prolate, while any outside the sheet makes it more oblate. Treating then the ideal cone as a skeleton and clothing it with matter within and without, a material double hollow cone may be made of the form of a diabolo spool but with the dynamical properties of a sphere. It is preferable, however, to make the spool with an axial hole and with a slight preponderance of moment of inertia about its rotational axis. It will then spin perfectly. It may, however, be easily adjusted by the insertion of a stick which is cut off of such a length as to make the moments of inertia equal, as tested by suspension from a torsion wire. It is remarkable how close must be the adjustment before spinning becomes impossible. If the difference in periods of oscillation is as much as 1 in 35, spinning is quite easy; the periods should not differ more than 1 per cent. If the stick which makes the adjustment perfect when centrally placed is pushed out a little to one side, the adjustment is disturbed and spinning becomes easy, but now being unbalanced the spool, under the tilting couple of gravity and the string, precesses, and precesses faster as the rate of spinning is slower, so that if such a stick is made to project considerably on one side, it requires some dexterity to follow it through 180° or so before the proper spin is acquired, when the slower precession is easily followed. Mr. Boys considered the diabolo spool a useful addition to the apparatus of a classroom.

Prof. H. A. WILSON exhibited a Gyroscope illustrating Brennan's Monorailway.

A gyroscope is mounted in bearings so that it can spin about a horizontal axis and precess freely. The gyroscope is further mounted at the top of a rectangular framework. The axis of spin of the wheel is first placed at right angles to the plane of the framework. Attached to the vertical axis about which the precessional motion occurs is a short crank with a spiral spring attached, so that when precession occurs in any direction the precessional couple is increased and the top returns towards its initial position. The oscillations of the gyroscope about its mean position become continually larger until the stability of the arrangement disappears.

The CHAIRMAN remarked that the subject of gyroscopic action was an important one because gyroscopes would probably be used a great deal in the future. Although engineers knew all about translational motion, few were acquainted with rotational motion. The analogies between centrifugal force and the action of a gyroscope were very close. Prof. Perry then went into the case of steadying a rolling ship, and showed how the differential equations obtained could be modified to admit of easy solution.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 2nd inst., Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. Miss Joyce Burton Buckley, Dr. L. Gottschalk, Mrs. Robert Home, Dr. D. G. Johnstone, Sir Edwin Ray Lankester, K.C.B., Mr. S. F. G. Osborne, and Miss E. A. Stoney, M.A., were elected Members. Prof. L. J. Troost (Paris), Prof. Albin Haller (Paris), and Prof. Walther Victor Spring (Liege), were elected Honorary Members. The Special Thanks of the Members were returned to Lord Sanderson for his Donation of Five Guineas to the Fund for the Promotion of Experimental Research at Low Temperatures.

NOTICES OF BOOKS.

Inorganic Chemistry. By E. I. LEWIS, B.A. (Cantab.), B.Sc. (Lond.). Cambridge: The University Press. 1907.

IN this book the author endeavours to follow the strictly logical method of teaching chemistry, and to build up the science by studying each substance from the point of view of its composition first, using for all reactions only those compounds which have previously been thus studied. Thus the first chapter deals with the composition of water; then, hydrogen and oxygen being regarded as known, they are supposed to be supplied to the student as he requires them from a gas-holder, and the elements of the air are studied. Then common salt is electrolysed, and thus the learner gets acquainted with sodium and chlorine, and so on. A more philosophical aspect of chemistry is put before the student than is usual in elementary text-books, and on the whole fuller and more detailed information is given, which marks the book out as likely to be very useful for revision, and also to help the teacher to prepare his lessons. The discussion of the atomic theory is clear, and abstention from the use of formulæ and symbols until the theory is thoroughly understood is undoubtedly a wise procedure. Whether the logical method as expounded in the book is so far superior to all others as the author thinks, probably teachers will find they have reason to doubt. The electrolysis of water involves complex apparatus, and the help of an agent of which the beginner is quite ignorant, and from this point of view seems hardly suitable as an elementary study. However, in many ways the book is really valuable, and probably the students who use it will find it very helpful for preparation for an examination, for which it is often found that the modern text-book of elementary chemistry is quite useless.

Die Elektrochemische und Elektrometallurgische Industrie Grossbritanniens. ("The Electro-chemical and Electrometallurgical Industries of Great Britain"). By JOHN B. C. KERSHAW. Translated into German by Dr. MAX HUTH. Halle-a.-S.: Wilhelm Knapp. 1907.

IN this book a clear account is given of the present state of the electrochemical and electrometallurgical industries of Great Britain. The author has generally ascertained his facts from personal visits to the factories and works he describes, although he has to chronicle the exhibition of a decided disinclination on the part of many firms to provide him with information relating to plant, processes, and output. In spite of this difficulty he has succeeded in producing what must be regarded as the most complete short summary of the subject which has yet been published. The historical development of each branch is fully and interestingly treated, and where official data were for any reason unobtainable, estimates or information from other sources have been supplied. A tabular statement giving statistics as to the growth and relative importance of the different branches of the electrochemical industry would probably be found useful. An appendix to the book contains a literal translation into German of eleven of the most important English patents, beginning with Watts' method of decomposing salts and other substances, granted in the year 1851, and giving the specifications of patents taken out since that date relating to improvements in processes or apparatus.

Chlormethyl Sulphate.—J. Houben and H. R. Arnold. —Chlormethyl sulphate, $SO_4{<}^{CH_2.Cl}_{CH_3}$, may be prepared by passing vapours of sulphur trioxide over cooled monochlor methyl ether: $SO_3 + Cl.CH_2.O.CH_3 = CH_3.SO_4.CH_2.Cl$. The product of the reaction is a yellow or dark coloured heavy oily liquid. It can be purified by distillation *in vacuo*, and it is then found that the pure substance is a liquid of specific gravity 1·473 at 18°. It is fairly stable in air, and slowly decomposes with water, giving methyl sulphuric acid, formaldehyde, and hydrochloric acid.—*Ber.*, xl., No. 15.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlv., No. 19, November 4, 1907.

Disecondary Butylene Monochlorhydrine. — K. Krassousky.—Five years ago the author described a method of preparing $H_3C—\underset{\underset{OH}{|}}{CH}—\underset{\underset{Cl}{|}}{CH}—CH_3$, which did not differ essentially from the process recently described by Louis Henry. This method was based upon the action of hypochlorous acid upon butylene, obtained either by allowing zinc ethyl to act on acetic aldehyde and then transforming the secondary alcohol thus prepared into iodide and decomposing with alcoholic potash, or else by adding zinc to butylene bromide in alcoholic solution.

Berichte der Deutschen Chemischen Gesellschaft. Vol. xl., No. 14, 1907.

Oxidation of Hydrazine.—A. W. Browne and F. F. Shetterly.—When hydrazine sulphate and ammonium metavanadate react in presence of sulphuric acid a secondary reaction takes place, which leads to the formation of hydrazoic acid and ammonia; the importance of this reaction depends upon the experimental conditions, such as the proportions of the substances, the temperature, the rate at which the metavanadate is added to the solution of hydrazine sulphate, and the amount of sulphuric acid present. The highest yield of hydrazoic acid yet obtained is 13·55 per cent of the theoretical yield according to the equation $2N_2H_4 + 2O = N_3H + NH_3 + 2H_2O$. The highest yield of ammonia is 21·3 per cent of the theory. The method of determining hydrazine by means of ammonium metavanadate proposed by Hofmann and Küspert is theoretically affected by a percentage error, which is numerically equivalent to the yield of hydrazoic acid, if the nitrometer method is used, but is much smaller with the oxygen method. The error with Lunge's nitrometer is about 4·5 per cent, and with the oxygen method about 1 per cent.

Reduction of Arsenic Tri- and Pentasulphides to Disulphide.—R. Ehrenfeld.—When a hydrochloric acid solution of stannous chloride acts upon arsenic tri- or pentasulphide they may be reduced to the disulphide according to the following equations:—

$$As_2S_3 + SnCl_2 + 2HCl = As_2S_2 + SnCl_4 + H_2S$$
$$As_2S_5 + 3SnCl_2 + 6HCl = As_2S_2 + 3SnCl_4 + 3H_2S.$$

This reaction explains the formation of a red precipitate when arsenic is detected in presence of tin. The reduction cannot be effected by the agency of other chlorides, such as arsenic trichloride, antimony trichloride, phosphorus trichloride, ferrous chloride, or chromous chloride. When carbon disulphide is heated in closed tubes with a hydrochloric acid solution of stannous chloride, most of the disulphide is unaltered after exposure to a temperature of 100° for twelve hours, although a small proportion of it undergoes the following reaction: $CS_2 + 2H_2O = CO_2 + 2H_2S$, and on opening the tube there is a distinct smell of sulphuretted hydrogen.

Dihydroxy - diaquo - diammino - chromic Salts, $\left[\begin{matrix}HO\\HO\end{matrix}Cr\begin{matrix}(OH_2)_2\\(NH_3)_2\end{matrix}\right]X$.—A. Werner and J. Dubsky.—By the action of bromine upon an aqueous solution of Reinecke's salt, $\left[Cr\begin{matrix}(SCN)_4\\(NH_3)_2\end{matrix}\right]K$, a green salt, dibromo-diaquo diammino-chromic bromide, $\left[Br_2Cr\begin{matrix}(OH_2)_2\\(NH_3)_2\end{matrix}\right]Br$, is obtained. When pyridine is added to a solution of this salt in water a crystalline precipitate of a monohydrate of dihydroxy - diaquo - diammino - chromic bromide, $\left[(HO)_2Cr\begin{matrix}(OH_2)_2\\(NH_3)_2\end{matrix}\right]Br + H_2O$, is formed. The extra molecule of water can be removed by drying at 60°. Other salts of the same constitution, which the authors have prepared, are the iodide and sulphocyanide, neither of which contains the additional molecule of water. The dithionate has the composition $\left[(HO)_2Cr\begin{matrix}(OH_2)_2\\(NH_3)_2\end{matrix}\right]_2S_2O_6 + H_2O$. No sulphate of this dihydroxy series could be prepared, all attempts to obtain it giving hydroxy-triaquo-diammino-chromic sulphate, $\left[(H_3N)_2Cr\begin{matrix}OH\\(OH_2)_3\end{matrix}\right]SO_4 + H_2O$. In acetic acid solution the following condition of equilibrium is established:—

$$\left[\begin{matrix}(H_2O)_2\\(H_3N)_2\end{matrix}Cr(OH_2)_2\right]\begin{matrix}(O.CO.CH_3)_2\\Br\end{matrix} \rightleftharpoons \left[\begin{matrix}(H_2O)_2\\(H_3N)_2\end{matrix}Cr(OH)_2\right]Br + 2HO.CO.CH_3.$$

The power of the hydroxyl of dihydroxy-diaquo-diammino-chromic bromide to bind acetic acid is so small that even in presence of a fairly large excess of the acid some of the unchanged hydroxy salt is still present, *i.e.*, a part of the tetraquo salt is hydrolysed to dihydroxy salt. No dihydroxy salt is precipitated when potassium bromide is added to a solution of the dihydroxy salt in a mineral acid; *e.g.*, hydrobromic acid.

Dihydroxy-tetrammino-platinum Compounds. — A. Werner.—The investigation of the dihydroxy-tetrammino-platinum compounds shows that phenomena which seem to point to isomerism are really to be ascribed to the existence of stable dimorphic forms. Thus, the sulphate, $[(HO)_2Pt(NH_3)_4]SO_4$, when prepared by one method, crystallises partly in the anhydrous form, and partly with 4 molecules of water; by another method the anhydrous form is always obtained. It is impossible to convert the anhydrous into the hydrated form by re-crystallisation, but by introducing crystals of the hydrated form into solutions of the anhydrous modification the transformation is readily effected. The electrolytic dissociation of the salt occurs as follows:— $\left[\begin{matrix}HO\\HO\end{matrix}Pt(NH_3)_4\right]X_2 \rightarrow \left[\begin{matrix}HO\\HO\end{matrix}Pt(NH_3)_4\right]^{++} + 2X^-$.

Hydroxy - pentammino - cobaltic Salts. — A. Werner. — These salts are formed by the action of ammonia upon aquo - pentammino - cobaltic salts, $\left[Co\begin{matrix}OH_2\\(NH_3)_5\end{matrix}\right]X_3 + NH_3 = \left[Co\begin{matrix}OH\\(NH_3)_5\end{matrix}\right]X_2 + NH_4X$. They have a basic reaction in aqueous solution. With ammonium salts the reverse action takes place:— $\left[Co\begin{matrix}OH\\(NH_3)_5\end{matrix}\right]X_2 + NH_4X = \left[Co\begin{matrix}OH_2\\(NH_3)_5\end{matrix}\right]X_3 + NH_3$. The author has prepared the iodide, chloride, bromide, nitrate, and dithionate of this series, and has found that they all contain one or more molecules of water, with the exception of the first. The salts do not behave like basic salts of the aquo-pentammino series, but their properties and reactions all show that they are hydroxy-pentammino salts. By the addition of hydrochloric acid the following reaction is produced: $\left[Co\begin{matrix}OH\\(NH_3)_5\end{matrix}\right]Cl_2 + HCl = \left[Co\begin{matrix}OH_2\\(NH_3)_5\end{matrix}\right]Cl_3$. The product when heated gives up water as follows:— $\left[Co\begin{matrix}OH_2\\(NH_3)_5\end{matrix}\right]Cl_3 = H_2O + \left[Co\begin{matrix}Cl\\(NH_3)_5\end{matrix}\right]Cl_2$, and the chloro - pentammino - chloride by the action of concentrated ammonia is converted into hexammino-chloride, $\left[Co\begin{matrix}Cl\\(NH_3)_5\end{matrix}\right]Cl + NH_3 = [CO(NH_3)6]Cl_3$. When the actions of the aqueous solutions of the chlorides of the four series upon litmus are compared the following results are obtained:—

$\left[Co\begin{matrix}OH\\(NH_3)_5\end{matrix}\right]Cl_2$	$\left[Co\begin{matrix}OH_2\\(NH_3)_5\end{matrix}\right]Cl_3$	$\left[Co\begin{matrix}Cl\\(NH_3)_5\end{matrix}\right]Cl_2$	$[Co(NH_3)_6]Cl_3$
Basic.	Acid.	Neutral.	Neutral.

MISCELLANEOUS.

Physical Society Exhibition.—At the Exhibition to be held by the Physical Society on Friday evening, December 13th (from 7 p.m. to 10 p.m.) at the Royal College of Science, South Kensington, the following firms will be exhibiting:—Messrs. R. and J. Beck, Ltd.; Cambridge Scientific Instrument Co., Ltd.; Casella and Co.; A. C. Cossor; Crompton and Co.; Elliott Bros.; Everett, Edgcumbe, and Co.; Evershed and Vignoles, Ltd.; Clark Fisher and Wadsworth; Gambrell Bros.; J. J. Griffin and Sons; A. Hilger, Ltd.; Leslie Miller; Nalder Bros. and Co.; Nalder Bros. and Thompson, Ltd.; Newton and Co.; R. W. Paul; James Pitkin and Co.; Ross, Ltd.; Alexander Wright and Co.; and also the Meteorological Office. From the Programme, of which we have received an advance proof, there appear to be many items of considerable interest to both Physicists and Electrical Engineers. We understand that invitations have been given to the Institution of Electrical Engineers, the Faraday Society, the Optical Society, and the Röntgen Society. Admission, however, except to Fellows of the Physical Society, will be by ticket only, and therefore Members of the Societies just mentioned desiring to attend the Exhibition should apply to the Secretaries of the Society to which they belong.

Royal Institution.—The following are the Lecture Arrangements at the Royal Institution before Easter:—Sir David Gill, a Christmas course of six illustrated lectures on "Astronomy, Old and New," adapted to a juvenile auditory; Dr. A. A. Gray, two lectures on "The Internal Ear of Different Animals"; Prof. F. J. Haverfield, two lectures on "Roman Britain—(*a*) Its Frontiers and Garrison, (*b*) Its Interior Civilisation"; Prof. W. Stirling, six lectures on "Membranes, their Structure, Uses, and Products"; Dr. E. A. Wallis Budge, three lectures on "The Egyptian Sudan, its History, Monuments, and Peoples, Past and Present"; Prof. W. W. Watts, two lectures on "(i.) The Building of Britain, (ii.) Recent Light on Ancient Physiographies"; Major Martin Hume, three lectures on "The Story of the Spanish Armada"; Prof. W. Somerville, two lectures on "Wood, its Botanical and Technical Aspects"; Prof. Sir John Rhys, two lectures on "Celtic": Mr. R. T. Glazebrook, two lectures on "Physics"; Mr. R. Lydekker, two lectures on "(i.) The Animals of Africa, (ii.) The Animals of South America"; Prof. Gisbert Kapp, "The Electrification of Railways"; Mr. Lionel Cust, two lectures on "Anthony Van Dyck"; Mr. Selwyn Brinton, three lectures on the "Art of Florence"; and Prof. J. J. Thomson, six lectures on "Electric Discharges through Gases." The Friday Evening Meetings will commence on January 17, when Prof. T. E. Thorpe will deliver a Discourse on "The Centenary of Davy's Discovery of the Metals of the Alkalis." Succeeding Discourses will probably be given by Colonel David Bruce, Prof. E. Rutherford, Mr. Humphry Ward, Dr. C. W. Saleeby, Sir Oliver Lodge, Prof. W. A. Bone, Prof. J. Milne, Prof. A. E. H. Love, The Hon. R. J. Strutt, Lord Montague of Beaulieu, Prof. J. J. Thomson, and other gentlemen.

MEETINGS FOR THE WEEK.

MONDAY, 9th.—Society of Arts, 8. (Cantor Lectures). "Theory of the Microscope," by Conrad Beck, F.R.M.S.

WEDNESDAY, 11th.—Society of Arts, 8. (Aldred Lecture). "Radioactive Phenomena," by Sir William Ramsay, K.C.B., &c.

THURSDAY, 12th.—Society of Arts, 4.30. "Big Game in India," by R. Gilbert, F.Z.S.

FRIDAY, 13th.—Society of Arts, 8. (Shaw Lecture). "Industrial Poisons—Lead and Phosphorus, with Special Reference to the Manufacture of Lucifer Matches," by Prof. Thomas Oliver, M.D.

—— Physical, 7. Exhibition of Electrical, Optical, and other Physical Apparatus, in the Physics Laboratory, Royal College of Science, Imperial Institute Road, South Kensington.

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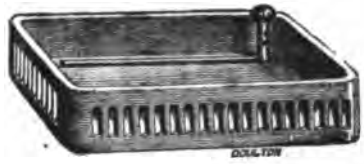

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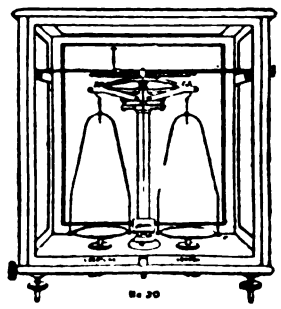

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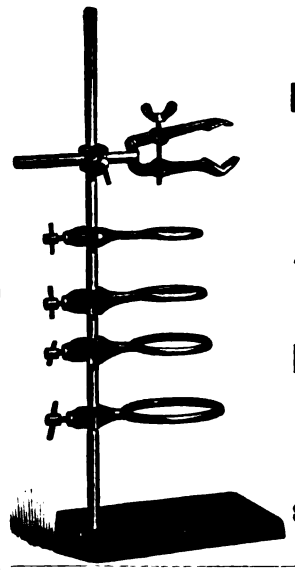

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THE CHEMICAL NEWS.

VOL. XCVI., No. 2507.

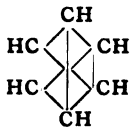
THE ORIGIN OF COLOUR IN ORGANIC COMPOUNDS.

By PERCY MAY.

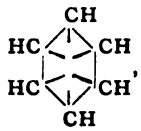
PART I.

THE study of the cause of colour in organic compounds is of necessity a modern one. The vast majority of coloured compounds are of the "aromatic series," and before the time of Kekulé we had practically no knowledge of the constitution of these bodies. It is true that there are coloured substances other than those of the aromatic series, but they are either complex bodies, such as murexide (which also has a cyclic structure), or substances such as iodoform, the colour of which is probably due to the mere *presence* of the iodine atoms, rather than to the *linkages* of the atoms in the molecule, and so lies outside the scope of the theories for *organic* compounds in particular.

It was in 1865 that Kekulé brought forward his well-known ring formula to express the constitution of benzene, and it is difficult to over-estimate the importance of this conception. Since that time many slight modifications have been proposed, such as that of Claus (diagonal) and

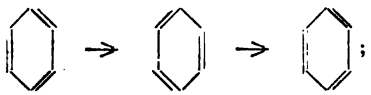


Claus.



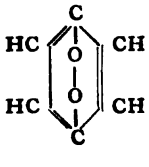
Baeyer-Armstrong.

Baeyer-Armstrong (centric), but these have no particular advantage over the Kekulé formula, which, as originally given, is a *dynamic* and not a static one, the so-called "double-bonds" being regarded as continually revolving round the molecule,—

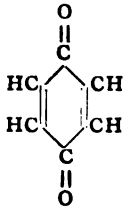


the original reason for this hypothesis being that if the "double-bonds" were fixed, then there would be four di-substitution products of benzene, instead of three, as is actually the case. The importance of this dynamic view in connection with colour theories will be seen later, but it may be as well to state at this point that these theories necessitate a vibration in the benzene molecule. Collie has devised a space formula for benzene, according to which the Kekulé centric, diagonal, and many other suggested formulæ for benzene represent only different phases in the vibration of the molecule.

Soon after Kekulé's epoch-making theory, much work was done on the synthesis of various colouring matters



I.

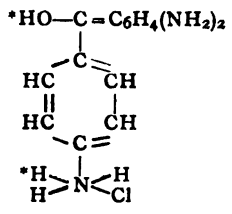


II.

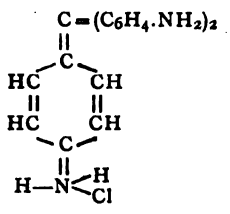
—notably that of alizarin by Graebe and Liebermann—but there is not much to chronicle concerning colour theories till 1888, when Nietzki and Armstrong advocated the quinonoid structure for coloured aromatic compounds. Qninone has the formula $C_6H_4O_2$, and two constitutions have been devised to account for its behaviour—the peroxide formula of Graebe (I.) and the ketonic formula of Fittig (II.).

It seems probable that the substance is tautomeric, but its constitution is usually represented by the latter formula, which is taken as the starting-point of the generalisation that coloured bodies have a quinonoid structure :—

The reason for this theory is best seen by the study of a few characteristic examples. The colour base of pararosanilne is $C(OH)(C_6H_4.NH_2)_3$, and is colourless; this forms a colourless salt by the addition of one molecule of HCl which has the Formula A.



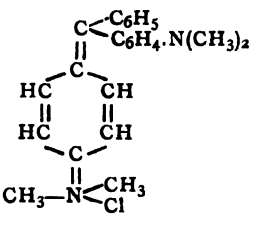
A.



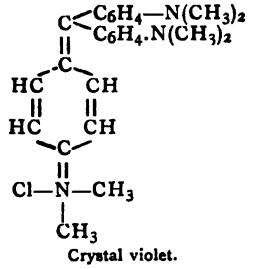
B.

(The asterisks denote the groups which split off to give B).

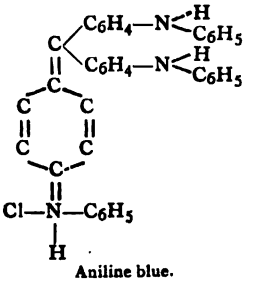
This salt is very unstable, and it readily loses one molecule of H_2O, and gives the brilliant magenta dye (B). In a similar way, other dyes derived from $HO.C(C_6H_5)_3$ are salts formed with elimination of water, and may be given a quinonoid structure; examples are :—



Malachite green.



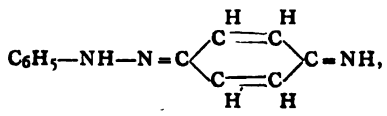
Crystal violet.



Aniline blue.

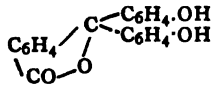
Another set of brilliantly coloured substances is formed by the azo-compounds, many of which are commercially used as dyes. As an example, we may take amidoazo-benzene (aniline yellow). Its synthesis suggests the

formula $C_6H_5—N=N—C_6H_4.NH_2$, but its reactions are just as well expressed by the formula—

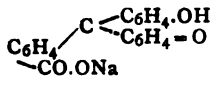


where we again have the quinonoid structure.

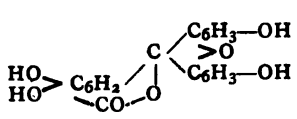
It is a well-known fact that phenolphthalein is colourless in neutral or acid solution, but becomes intensely coloured with a trace of alkali. This is accounted for by the fact that the substance itself is not a true acid, but has a lactone formula,—



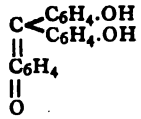
while in the coloured salt the lactone ring is opened out-giving a quinonoid structure :—



Similarly, we have for the fluoresceins the formulæ—

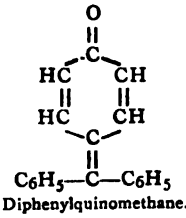


Type of colourless derivative. } Flouresceïn. { Type of coloured derivative.

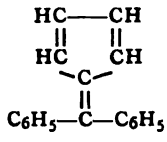


Aurine.

Aurine also forms a hydrochloride, and this according to Baeyer and Villiger (*Berichte*, 1904, lvii., 2848) is also of the quinonoid type, the oxygen being tetravalent as in dimethylpyrone salts and those of other "oxonium" bases. At the same time, these authors bring forward arguments in favour of Fittig's formula for quinone, and they point out how diphenylquinomethane (the parent substance of aurine) only differs from diphenylfulvene by a single carbonyl group :—

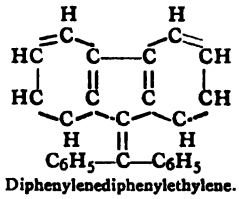


Diphenylquinomethane.

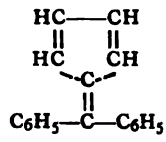


Diphenylfulvene.

The latter is deeper red than the former, and therefore the carbonyl group by itself does not appear to be a chromogen as is often supposed. Baeyer and Villiger account for this by saying that the addition of the carbonyl group causes the five-membered ring to become a six-membered or benzenoid ring, thus weakening the aliphatic nature of the "double bonds," and so causing the molecule to approach more nearly to the type of benzene, with simultaneous loss of colour. This view is at first sight strengthened by the relation between diphenylenediphenyl-ethylene and diphenylfulvene :—



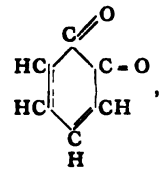
Diphenylenediphenylethylene.



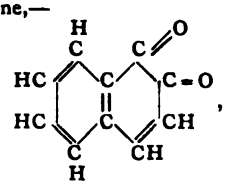
Diphenylfulvene.

In the former, both the ethylenic double bonds have become part of aromatic rings, and simultaneously the colour has vanished. Baeyer and Villiger, however, offer no explanation of the fact that a solution of diphenylenediphenylethylene is yellow, as is also the molten substance. The explanation of this is probably that the diphenylenediphenylethylene is really coloured, and that the colourless solid is a polymer of it. This of course destroys the value of the relationship, and leaves the whole question still open, but the above facts are worth citing as they show the necessity for great caution when proposing theories of colour. The properties of the above mentioned substances and of bidiphenylene-ethylene are being investigated at present by the author of this paper, in order to shed further light on the subject.

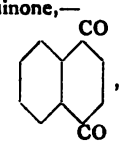
So far consideration has only been given to the para-quinones, of which ordinary quinone is the type. The *simple* orthoquinone—



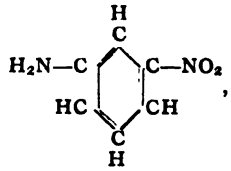
was for long unknown, but it has recently been prepared by Willstätter and Pfannensteil (*Berichte*, 1904, xxxvii., 4744), who isolated it in the form of light red plates. β-Naphthoquinone,—



is far better known, and is also a red crystalline body, the corresponding paroquinone,—



being yellow, like ordinary quinone. This is quite a general fact, the simple paraquinones being yellow and the orthoquinones red. Although the consideration of ortho-quinones extends the usefulness of the theory of quinonoid structure, yet there are still many instances where it cannot be applied. For example, the brilliant yellow colour of metanitraniline,—



cannot be accounted for by the usual theory of quinonoid structure. Another weakness of the quinonoid theory in its original form, is that it does not attempt to explain *why* quinonoid bodies should be coloured.

The answer to this question will be discussed in Part II., but before passing on mention should be made of Witt's theory of chromophores, and other similar theories, according to which colour is due to certain chromophoric groups, such as:—

1. $CO—C=C—C=C$
2. $—CO—CO—C=C$
3. $—C=C—CO—C=C$
4. $CO—C=C—CO$

It should be noticed that 1 and 2 contain the same groupings as the orthoquinones, and that 3 and 4 have the same groupings as in paraquinones. Witt, from his investigations of nitrogen compounds has proposed other "chromophores" to account for their colour. Thus, toluylene blue, $N(CH_3)_2—C_6H_4—N=CH—C_6H_3(NH_2)_2$, contains the chromophore $—N=\overset{H}{\underset{|}{C}}—$, which Witt regards as a link between that of rosaniline, $\equiv C—NH$, and that of the azo-series, $—N=N—$. This theory is simply of use to co-ordinate facts, and it does not appear to be very fertile or useful when compared with the other theories of colour.

We have now considered the more or less empirical theories that have been brought forward to "explain" the cause of colour, but it will be seen that none of these are very complete or satisfactory. In Part II. will be considered the recent developments of the subject which tend to explain the true physical meaning underlying the theory of quinonoid structure, and which promise to throw a most important light on the problems of chemical structure in general.

(To be continued).

THE NATURE OF THE NON-ABSORBENT ZONES MADE BY INK BLOTS ON BLOTTING-PAPERS.

By CLAYTON BEADLE and HENRY P. STEVENS.

ALTHOUGH considerable notice has been taken of the non-absorbent zone produced by ink on certain makes of blotting-paper, no systematic attempt has been made to ascertain the *cause* of the non-absorbency of this zone (see Beadle and Stevens, *Paper and Pulp*, Dec., 1904, p. 717).

Throughout this work we have as in former papers used Stephens's blue-black ink as a standard quality, and always from a freshly opened bottle. We consider this as a more practical test than if use had been made of a standard record ink.

When ink, such as Stephens's blue-black ink, is allowed to flow on to a sheet of blotting-paper held horizontally, say in quantities or 0·5 cc. at a time, and when the blot after it ceases to spread is held up to the light, an outer ring or zone will be noticed with several of the best makes of blotting both before and after such blots have been allowed to dry. If after drying such blots fresh ink be drawn across or dropped upon these blots by means of a pen or pipette, the outer zone will be found to have lost its absorbency for ink, although the inner portion still retains its absorbency more or less. The percentage that the width of this zone bears to the total diameter of the blot gives a figure which is fairly constant with given makes of blottings if tested always with the same kind of ink, and this figure since our first published researches has been recognised as a test for absorbency both in this country and in Germany.

As a more accurate means of recording this loss of absorbency (see Beadle and Stevens, *Paper and Pulp*, Dec., 1904, p. 721), we prefer now to express the ratio in relative areas of the non-absorbent zone to that of the total areas of the blot produced. The appearance as well as the width of the zone varies with any given ink for different blottings, or with different inks when applied to any particular make of blotting.

It has been assumed that the gum of the ink is responsible for the production of this non-absorbent zone. If such had been the case, digesting ink blots so produced in warm water in which the gum would dissolve would remove the zone, but finding that the zone was not diminished by this treatment, at least on those blots that had been produced for some time, we looked to the iron salts of the ink as the probable cause of the difficulty. (Communication to the Society of Pulp and Paper Chemists, Nov., 1907).

Before describing the results of our recent work we must first refer to what is now a matter of history. It has long been known to us that certain basic constituents, notably the lime salts contained in the paper, are the cause of certain papers giving a non-absorbent zone.

This matter was fully treated of in our original paper (*Paper und Pulp*, Dec., 1904, p. 723), where we gave the analyses of the constituents of the ash of a number of blottings. We were therefore somewhat surprised to find the following statements on page 184 of the recently published third edition of Herzberg's "Papierprüfung." After describing our zone test and the results of a number of determinations made in the Materialprüfungsamt, Prof. Herzberg discusses the cause of the impervious zone, and refers to question of lime salts in the paper, stating that our view of their primary connection with the impervious zone cannot hold water and may be dismissed *without the need of making anatyses*. He arrives at this conclusion from certain deductions based on a relationship between the ratio of rise and percentage of impervious zone. From an examination of his figures we very much doubt if any such relationship exists, at any rate it is certainly subject to many exceptions, in particular as regards rag papers, where no relation can be traced of the kind mentioned. Thus if we take the table given on p. 182 of Herzberg's "Papierprüfung" and pick out the rag papers and compare them with one another, we obtain the following figures:—

Herzberg's reference number.	Per cent ash.	Mean rise in ten minutes.	Per cent width of zone.		
			Alizarin ink.	Iron-gallic acid ink.	Mean with both inks.
4	1·0	132	7	7	7
5	0·8	121	8	10	9
8	0·8	85	6	10	8
9	2·8	68	1	10	5·5
10	0·8	59	10	12	11
12	3·0	44	1	10	5·5
13	12·8	34	1	10	5·5
14	1·0	31	12	13	12·5

We think that a careful study of the above figures will not reveal any very simple relationship between the mean rise in ten minutes and the percentage width of zone whether the figures for either of the two inks to be taken or the mean of both. Yet according to Herzburg ("Papierprüfung," 3rd edition, p. 183) it usually happens that those papers giving the greatest mean rise yield the widest zones. (It will be seen that in the above table No. 4 giving the greatest rise gives a relatively narrow zone, while No. 14 with the least rise gives the widest zone.) As we have attributed the cause of the zone to a relatively high percentage of basic constituents, in particular lime in the paper, Herzberg arrived at the conclusion that papers giving the greatest mean rise would have the highest percentage of lime, an assumption which he states will not hold water. Having arrived at this conclusion in this curiously roundabout manner, he feels quite satisfied in dismissing our explanation of the cause of the zone without troubling to make analyses which he thinks would be quite unnecessary.

Under these circumstances we feel that it is necessary to refer again to the figures we previously published in *Paper and Pulp*, Dec., 1904, p. 723, showing that those papers examined giving a wide zone contained relatively large proportions of lime, and those giving a narrow zone only traces of lime.

As to wood pulp a sample sheet zoneless-to-ink will yield a blotting also zoneless-to-ink if basic mineral matter be excluded. We have tested reveral samples of wood pulp, and found them zoneless-to-ink. The rate of rise of water in any blotting depends on the *make* of the paper. One of us proved this with commercial English makes. The rate of rise varied as the percentage of air-space; in other words, the greater the sponginess the greater and quicker the absorbent qualities (Clayton Beadle, "The Fibrous Constituents of Paper," *Technics*, vol. i., p. 573). Some materials may be so manipulated in the process of manufacture into paper as to give a high figure for the rate of rise, but at the expense of other important qualities (*i.e.*, felting qualities), but with the same material made into a good felted sheet the rise may be, and often is, much less.

That the formation of an impervious zone is primarily due to the basic constituents of the paper may be shown by a very simple experiment. Take a sheet of blotting giving a non-absorbent zone of considerable area and digest it for a short while in a weak solution of an acid to remove the basic constituents, wash well with distilled water, and dry. The paper will now be found to yield no non-absorbent zone, or, as we may shortly describe it to be, zoneless-to-ink. Soaking in hard water and drying is sufficient to destroy the zoneless-to-ink character of the paper again, or by the use of lime-water a zoneless-to-ink paper may be converted into one giving a wide zone. A number of other basic constituents have been added to zoneless-to-ink paper, giving rise to zones varying according to the amounts added. If a paper containing in addition to lime salts, iron, alumina, and other bases, either as oxides or hydroxides or basic salts, be treated carefully with weak acid so as to remove only the lime salts, the tendency to formation of zone is diminished, but not entirely removed; that which remains is due to bases other than lime.

We think that Prof. Herzberg must admit that these simple experiments confirm in all respects the results of analyes of the ash referred to above, and point to the primary importance of basic substances such as lime in the formation of the impervious zone. If further confirmation were desired, we may state that we are patentees of a process for the production of zoneless-to-ink paper which has been worked successfully in a mill, and is still giving satisfactory results, and that our patent is based on the production of a blotting-paper from which the basic mineral constituents are removed or rendered inactive.

Before proceeding further we may therefore take it as proven that a zoneless-to-ink blotting is free, or practically so, from basic mineral constituents, while a paper giving a zone will be found to contain a larger or smaller proportion of basic substances or bodies capable of neutralising acids, and that the formation of a zone is a quality entirely apart from fibrous constituents or felting qualities, and, furthermore, that the production of zone is a quality entirely apart from bibulous qualities as measured by rate of rise in water.

To investigate the action of iron salts on blotting-paper producing zones we treated a paper known to give a wide ink zone by dropping on to its surface ferric chloride solutions of different concentrations.

(It is worthy of note that the imperviousness of a zone is greater in old blots in comparison with freshly prepared ones, and when testing the width of zone on blots freshly prepared. And again after two and a-half years we have found a distinct increase in the width of imperviousness due to ageing).

It was found that except in the case of very concentrated solutions tested immediately after drying, an impervious zone or ring was produced on the margin of the blot. The loss of absorbency produced by blots of very strong ferric chloride solution immediately after drying in an oven, is to be ascribed merely to a dried residue of a high concentration being produced in the paper, and has nothing to do with the impervious zone above referred to. This loss of absorbency, due to high concentration, disappears when the blots take up moisture from the atmosphere.

If a zoneless-to-ink paper is treated as above described with ferric chloride solutions of different concentrations, it is found in all cases to be zoneless to ferric chloride. If, however, the same paper be artificially loaded with carbonate of lime it will produce an impervious zone with ink, and it will be found that as the concentration of the ferric chloride solution is reduced, a zone is produced which within certain limits varies in width inversely as the concentration of the ferric chloride solution. When the concentration of the ferric chloride is reduced to that of the iron salts normally contained in ink, the zone is at least as wide as the zone produced by ink itself. If now any commercial paper be chosen which is known to produce a zone with, say, Stephens's blue-black ink, it will also be found to produce a zone with dilute ferric chloride solution, and the area of the zone so produced will vary with the concentration of the ferric chloride solution.

When ferric chloride blots so produced are dried, and ink is applied to them, it will be found that both the inside and outside of the zone is pervious to ink, whereas the zone itself is impervious, corresponding in this respect to a zone produced by an ink blot similarly dried down and tested. The ferric chloride blots will be found to possess the colour of ferric chloride in that portion of the blot surrounded by the zone, but the zone itself will have the buff colour of ferric hydroxide or basic ferric salt.

When either ferrous or ferric sulphate, with or without the addition of sulphuric acid, is applied to a blotting-paper in a similar manner to the above, it will be found that these salts behave in a similar manner to ferric chloride.

In the case of dilute ferrous sulphate with a small addition of sulphuric acid, which more or less represents the condition of iron in freshly made ink, the effect produced well illustrates the formation of a basic ferric compound or salt in that part of the paper which ultimately becomes a non-absorbent zone. On allowing 0·5. cc. of such a solution to spread in the form of a blot on a zoneless-to-ink blotting-paper, and allowing to dry no zone effect is produced on the paper. If, however, the same experiment be made with a blotting which gives an ink blot with a zone, it will be noticed that as the wetness ceases to spread a change of colour takes place round the outer edge, and when dry there is found to be a buff-tinted impervious zone with a *colourless* and absorbent interior portion. In the case of a blot made with a *neutral* solution of ferrous sulphate, the interior portion is partially non-absorbent.

If, now, with one or other of the above salts we are correct in attributing the non-absorbency of the zone to ferric hydroxide or basic ferric compound, treatment of the blot so produced in water would remove the soluble iron salts from the interior of the blot and leave the insoluble iron in the zone.

This was found to be the case. Thus, a ferric chloride blot was produced, dried down and digested in hot water for the removal of the soluble iron salts, and again dried and tested. It was found that the zone was not removed, and remained impervious, whereas that portion enclosed by the zone had lost its iron salts.

To test this point further a blot was made in a similar manner, but not dried down before immersion in water. Even under these circumstances a non-absorbent zone was produced which withstood the digestion with water.

The increase of the non-absorbent zone due to dilution can be demonstrated by making a small concentrated blot, say, of ferric sulphate, to the centre of which is applied, drip by drip, distilled water from the nozzle of a wash

bottle. The original blot may have given little or no zone, but as the blot already formed is caused to spread the zone is increased, and is rendered visible by the appearance of reddish hydroxide or basic ferric salt, which after drying and testing with ink is found non-absorbent, whilst the interior of the blot retains its absorbency.

When a blot is produced by ferric chloride of an intermediate concentration (say, 15 per cent), which on first drying and testing shows a visible and non-absorbent zone, the same zone is found to have wholly or partially disappeared in about twenty-four hours, due to the fact that the ferric chloride being hygoscopic absorbs sufficient moisture to cause it to go into solution, and so dissolve the freshly deposited ferric hydroxide. With solutions of ferric chloride of lower concentrations, such as those which do not produce any visible hygroscopic effect, and remain dry to the touch, the visible and non-absorbent zone remains permanent.

The loss of zone with intermediate concentrations when using ferrous sulphate, even with the addition of a small amount of acid, is not noticeable. This we attribute to the fact that the deposits are non-hygroscopic.

The reason of the deposition of the ferric hydroxide or basic salt from the soluble iron salts is not to be accounted for as a process of dissociation, because these iron salts do not show a non-absorbent zone, except in contact with paper containing certain basic constituents capable of depositing ferric hydroxide or basic salts by combination with the acid radicle. When a few drops of soluble iron salts are placed on such a paper, at first the acid constituents of the blot are in excess, but as the blot spreads the basic constituents of the paper begin to predominate, from which point outwards ferric hydroxide is deposited and the non-absorbent zone is produced. It consequently stands to reason that the less concentrated the iron salt the sooner the basic constituents of the paper begin to predominate, and the wider the zone produced.

Ferric hydroxide or a basic salt being, as it were, deposited *in situ*, and probably in a colloidal condition, is capable of sizing the paper and so rendering it ink-proof.

To ascertain whether the iron of the ink behaves in a similar manner, and accounts for the production of the non-absorbent zone, we took some ink blots produced by discharging 0·5 cc. of Stephens's blue-black ink on a paper giving rise to a wide zone. Portions of blots so produced after drying were bleached by immersion in strong bleaching-powder solution, which discharges the colouring matter of the ink, leaving the iron as a residue in the paper.

If, now, a blot so bleached out, and after immersion in water be held up to the light, it will be seen that the centre of the blot, as well as the body of the paper itself, is thoroughly wetted through and transparent, whereas the non-absorbent zone remains opaque and of about the same degree of opacity as the dry blotting-paper in consequence of its refusal to absorb water. Figure 7 shows a print produced from a blot while still wet after bleaching out the colouring matter of the ink. This photograph is a *negative* produced by contact with *wet* blotting-paper, and taken by transmitted light to show the relative wetting qualities of the zone and the body of the paper. The zone remains white because when wetted it remained as opaque as a dry sheet. The interior of the blot is in reality as transparent as the body of the paper, but does not appear so on the photograph, because the yellow colour of the iron salt it contains intercepts some of the actinic rays.

Viewing one of these wetted bleached-out blots by reflected light, the non-absorbent zone will appear as an incrustation. For some reason or other the surface of the zone does not frequently show the characteristic brown colour until the blot is dried down by heat, when it begins to develope, but the brown colour can be produced by moistening with ammonia.

Before drying the colour may be described as a dirty white, probably due to some basic salt, which partially decomposes on drying down or on treating with a base with the production of ferric hydroxide.

There is something peculiar about this deposit producing the non-absorbent zone which we have not yet fully accounted for, and which we are still investigating.

The non-absorbent zone of the bleached-out ink blot is still as impervious to ink as before bleaching out.

If the bleached-out product after prolonged soaking in water is brought upon a glass plate whilst still wet, and ink applied on either side of the zone, the ink flows on either edge without passing over it, thus showing the zone is still non-absorbent even after bleaching and prolonged wetting.

If a bleached-out blot after washing and drying is placed for a time in a dilute solution of potassium ferrocyanide to which is added a few drops of hydrochloric acid, the interior immediately developes a blue colour, whereas the zone retains its yellow tint and remains unacted upon, thus showing the difference in the condition of the iron residue from the ink contained in the interior of the blot, and that constituting the impervious zone.

Thinking that there would be a difference in the solubility of the iron contained in the interior of the blot as compared with that contained in the zone, a bleached-out blot was treated with a 10 per cent HCl solution in the cold for a few minutes, and then washed. The iron in the interior of the blot was found to have gone into solution, whereas the iron contained in the zone was still unacted upon. This is further rendered evident by subsequently developing the above mentioned blot in potassium ferrocyanide.

If now a part of the same blot be again treated with strong hydrochloric acid, the zone gradually loses its non-absorbent nature, first of all becoming of the colour of ferric oxide, and then developing a blue colour with potassium ferrocyanide. If now the portion of the zone which has been converted into Prussian blue by this process is dried and tested with ink, it is found to be pervious, whereas that portion not so treated remains impervious.

Thinking that further light might be thrown upon the nature of the zone if the proportion of the iron contained in the interior and zone of the blot were separately determined, we took two blots produced on paper giving a wide zone, one of these blots A was slightly moistened so as to admit of the interior absorbent portion being detached from the exterior non-absorbent zone, and the body of the paper surrounding the zone was also moistened in order that it might be separated in the same manner. By this means a ring consisting of the non-absorbent zone was completely detached from the interior of the blot and the body of the paper, so that each could be separately examined.

The zone and interior of blot A were dried, weighed, ignited, and the iron in the ashes of each determined.

Zone of Blot A contained	..	4·6 per cent Fe.
Interior of Blot A contained	..	1·5 do.

Thus it will be observed that the non-absorbent zone which from its colour does not appear to contain anything like so much ink as the interior portion, as a matter of fact contains three times the percentage of iron as compared with the interior. It should be observed that on drying, and before ignition, the ring weighed 0·195 grm., and the interior 0·329 grm.; therefore the ring as detached constituted 37 per cent by weight of the blot and the interior 63 per cent.

We thought it advisable to take a similar blot, and to digest it for some time in hot water before detaching the ring from the interior so as to remove all the soluble constituents of the ink. This was accordingly done, and the zone separated from the interior as above described. The zone and the interior on drying were found to weigh as follows:—

Blot B.

Zone	.. .. ..	0·169	grm.
Interior	.. .. ..	0·249	„

The total weight of the blot so extracted was therefore

0·418 grm. as against the total weight of blot A unextracted of 0·524 grm.

The mean diameter of blot A was found to be 40·0 mm., the mean diameter of blot B to be 40·8 mm., the blots having been produced with 0·50 cc. of ink in each case. It may be assumed, therefore, that extraction with water reduced the weight of the blot by 20 per cent.

The ring and interior of extracted blot B were ignited and the iron determined in the ash, yielding the following figures expressed on the weight of the extracted blot.

Zone .. .. .. 4·6 per cent Fe.
Interior .. .. 2·0 „ „

If, however, the amount of iron found be expressed on the non-extracted blot in order to compare it with blot A, the following figures are obtained:—

Zone .. .. .. 4·0 per cent Fe.
Interior .. .. 1·5 „ „

It is evident, therefore, that the amount of iron contained in the blot is for the most part insoluble in water, and that the iron tends to migrate to the exterior of the blot during the formation of the impervious zone. It also appears that the interior of the blot contains iron easily soluble in dilute hydrochloric acid (even after bleaching out the tannic or gallic acid), whereas the iron of the zone is much less soluble, so much so that the one can be separated from the other by digestion in weak acid.

If that portion of the blot inside the zone be wetted and tested with litmus-paper, it is found to have a strong acid reaction, even when the blot is several years old, while the zone itself and the body of the paper outside the zone is without action on litmus-paper.

If the interior of the blot is cut out and placed in methyl orange solution it will be found to be strongly acid, while the zone is neutral and the body of the paper basic.

We think that we have sufficiently proved that the impervious zone produced by contact of writing ink with certain kinds of blotting-paper is due to the decomposition and deposition of the iron salts contained in the ink by certain basic constituents of the paper giving rise to the formation of ferric hydroxide, probably in colloidal form or other basic salts which filling the pores of the paper render it resistant to ink.

THE OXYGEN EQUIVALENT OF COCOANUT OIL.

By T. R. HODGSON, B.A., A.I.C.

The process used for the determination of the "oxygen equivalent" of cocoanut oil is that described in the previous paper, and again consists in the oxidation of the acids obtained after saponification and acidification.

Twenty samples of cocoanut oil were examined; they were all obtained in Birmingham, were all of the commercial variety, and were not subjected to any special purification. The following results were obtained:—

Sample.	$K_2Mn_2O_8$ used. Cc.	Sample.	$K_2Mn_2O_8$ used. Cc.
A.	25·0	L.	24·8
B.	21·6	M.	21·8
C.	21·8	N.	21·7
D.	26·8	P.	21·7
E.	21·8	Q.	21·8
F.	18·0	R.	21·8
G.	18·8	T.	21·7
H.	21·6	V.	21·2
I.	21·2	X.	21·7
K.	21·8	Z.	21·7

The number of cubic centimetres of tenth-normal potassium permanganate solution used multiplied by 4 gives the "oxygen equivalent." This, in the case of cocoanut oil, varies considerably, viz., from 72·0 to 107·2.

Sample.	Oxygen equivalent.	Sample.	Oxygen equivalent.
A.	100·0	L.	99·2
B.	86·4	M.	87·2
C.	87·2	N.	86·8
D.	107·2	P.	86·8
E.	87·2	Q.	87·2
F.	72·0	R.	87·2
G.	75·2	T.	86·8
H.	86·4	V.	84·8
I.	84·8	X.	86·8
K.	87·2	Z.	86·8

As will be seen from the above numbers, the variation is very considerable, but even the highest number obtained is very much lower than that of butter fat.

The average number obtained with the twenty samples examined is 88·66, leaving a difference of 80·54 between the average "equivalent" of the oil and that of butter fat.

The variation in the equivalent in the case of cocoanut oil is probably due to variation in the quality of the oil, as the price of the different samples varied considerably, ranging from 4d. to 2s. 8d. per pound. The influence of time on the oxidation is, as in the case of butter fat, variable up to about thirty minutes, but from thirty minutes up to one hour no oxidation seems to occur.

Time. Minutes.	$K_2Mn_2O_8$ used. Cc.	Oxygen equivalent.	
5	19·2	76·8	1·6
10	19·6	78·4	1·2
15	19·9	79·6	0·4
20	20·0	80·0	7·2
25	21·8	87·2	
30	21·8	87·2	
35	21·8	87·2	
40	21·8	87·2	
45	21·8	87·2	
50	21·8	87·2	
55	21·8	87·2	
60	21·8	87·2	

The numbers given above show that there is no regular increase in the equivalent; the large increase between twenty and twenty-five minutes is remarkable.

In my next paper the results of this and the previous paper (Chemical News, vol. xcvi., p. 273) have been applied to mixtures of cocoanut oil and butter fat in known proportions.

Analytical Department,
University of Birmingham.

Action of Sodium Dioxide and Barium Dioxide on Gold: Aurates.—Fernand Meyer.—When precipitated gold is added to fused sodium dioxide in a nickel crucible, nickel oxide is formed and some gold remains unaltered, while the solution obtained by adding water contains sodium aurate. Barium aurate can be prepared similarly. The action of sulphuric acid on an aurate gives auric acid. If auric acid is allowed to stand over sulphuric acid *in vacuo* and in the dark, its formula is found to be $Au_2O_3.3H_2O$. Sodium aurate may be prepared for analysis by adding a solution of soda to auric acid in absence of the carbon dioxide of the air. Strontium and calcium aurates may be prepared similarly. The formulæ of the compounds are $(AuO_2)_2Na_2$, $(AuO_2)_2K_2$, $(AuO_2)_2Ca$, $(AuO_2)_2Sr$, $(AuO_2)_2Ba$. They are stable on heating if dry. In solution they are decomposed by light and heat, the residue being violet-black Au_2O, which is soluble in hydrochloric acid. Sulphur dioxide reduces them to metallic gold.—*Comptes Rendus*, cxlv., No. 20.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 21st, 1907.

Sir WILLIAM RAMSAY, K.C.B., F.R.S., President, in the Chair.

THE PRESIDENT announced that the Society has received a portrait of Faraday and Daniell from Professor Meldola, and a silver medal from the Société Chimique de France, struck in commemoration of the recent Jubilee celebration.

Certificates were read for the first time in favour of Messrs. John Arthur Carpenter, B.A., New College, Oxford; Cyril Dickinson, B.Sc., F.I.C., Abbotsford, Holycroft Avenue, Hampstead, N.W.; Edward Mortimer Eagles, M.A., 5, Winsham Grove, Clapham Common, S.W.; Robert Cecil Gale, 38, Scarsdale Villas, Kensington, W.; George Neville Pingriff, B.A., 39, Hall Road, Handsworth, Staffs.; William Bayliss Shaw, Lonsdale House, Walsall; Harry Jackson Unwin, Market Place, Clay Cross, nr. Chesterfield; Herbert Walker, Whyttington, Station Road, Wealdstone, N.W.; Joseph Henry Williams, 27, Canbury Avenue, Kingston-on-Thames.

Certificates have been authorised by the Council under By-law I. (Par. 3) in favour of the following:—Edward Henry Croghan, care of Messrs. H. Eckstein and Co., P.O. Box 149, Johannesburg; Charles Thomas Foreman, Jamalpur, E.I.R., Bengal.

Of the following papers, those marked * were read:—

*225. "*Emulsions.*" By SPENCER PICKERING.

Paraffin oil, when churned with solutions of soap, glue, starch, albumin, &c., forms an emulsion which rises, like cream, to the surface of the excess of water, and contains from 65 to 82 per cent by volume of the oil. Close-packing of uniform globules would give an emulsion containing 74 per cent. The percentage of oil can be increased to 99 per cent, the emulsion then being practically solid. Emulsification seems to depend on the separation from the liquid of very minute solid particles which are attracted by, and surround, the oil globules, thus preventing them from coalescing. Any precipitated substance which is sufficiently finely divided will act as an emulsifying agent, but, after becoming agglomerated by drying, it loses this property. The basic sulphates of iron and copper are conspicuously good emulsifiers, and, when they are used instead of soap, it is possible to mix with the emulsions substances which could not be added if soap had been used; for example, sodium hydroxide. Solids which are not sufficiently fine grained to make true emulsions with oil, will sometimes make quasi-emulsions, in which the oil globules are merely entangled with the solid particles. In this case, dilution with water separates the oil from the solid, which is not the case with true emulsions.

DISCUSSION.

Dr. LEWKOWITSCH thought that all the phenomena mentioned by the author could be best explained by the colloidal state of the substances employed. He would therefore take exception to the explanation that the paraffin oil emulsified the soap solution, and would prefer to say that the soap solution emulsified the paraffin oil. Soap solutions were typical colloids, easily gelatinisable even in dilute solutions, and it was also well known how disconcerting soap solutions were once they had formed an emulsion with other substances, notably vegetable or mineral oils. The percentage (97) of paraffin oil in the emulsion shown appeared very high, and he therefore asked how much water and how much soap, presumably soft soap, were in the remaining 3 per cent. Soap solutions emulsified, not only paraffin oils, but also alcohol, and notably very large amounts of water.

The ferric sulphate and also the copper salt mentioned by the author were known to occur in the colloidal state, and therefore their property of forming emulsions would explain the phenomena referred to. The experiments shown with the emulsions produced by soap would fall in well with that explanation. On adding hydrochloric acid, the soap was decomposed with the formation of free fatty acids. These, at any rate those formed in the given case, were not colloids, and therefore the emulsion was "broken" at once, and water separated, the fatty acids remaining dissolved in the petroleum. The fact that caustic soda "broke" the emulsion was also easily explained, as caustic soda "salts out" soaps; that is, precipitates them from their colloidal solution, and therefore water must separate out again. That in the experiment with lime no emulsion was formed could also be readily explained by adopting his view, for under the given conditions lime would not behave like a colloid.

Mr. J. CASTELL-EVANS thought that surface-tension had a great deal, if not all, to do with the formation of emulsions, and that many finely-divided substances may be found which will induce the formation of emulsions of petroleum and water. He instanced a case, falling within his own personal observation, in an attempt at "oil concentration" of the metalliferous contents of some calcined tailings. These tailings consisted largely of ferric oxide, and, after calcination, had been "weathered" for many years. On shaking up with water and mineral oil of about 0·89 sp. gr., the silicious matter, as expected, sank to the bottom of the cylinder; so also did the coarser particles of ferric oxide, whilst the finer particles of the oxide remained in the oil, forming apparently a true emulsion. This "emulsion" did not make the sides of the cylinder oily, and remained persistent for many months. The coarser particles of the oxide did not present a sufficiently large surface, in proportion to their mass, to be retained by the petroleum.

Dr. BORNS inquired whether the author had succeeded in obtaining any emulsions of oil and pure water. K. Beck (*Zeit. Phys. Chem.*, 1907, lviii., 409) had found that the viscosity of water was not affected when the water was churned with oil. When he prepared an emulsion of oil and water by rubbing the oil with some gum arabic in a mortar and adding water, however, the viscosity of the water was increased.

The PRESIDENT suggested that the suspended particles in an emulsion may be similarly electrified, and so repel each other and fail to coalesce. No doubt this phenomenon is closely connected with surface-tension phenomena. The addition of electrolytes may possibly discharge the electrified particles and cause coalescence.

Mr. PICKERING, in reply, stated that the strongest emulsion which he had obtained contained only 1 per cent of a 1 per cent soap solution. The action of soap as an emulsifying agent was very uncertain, but that was not the case with insoluble emulsifiers. Such colloids as he had tried did not emulsify, but, on the contrary, became gelatinised. The basic sulphates were clearly not colloids; the particles composing them could be seen under the microscope. No doubt surface-tension played an important part in emulsification, but that offered no explanation of the phenomenon. Electrolytes, as such, had no effect on emulsions.

*226. "*Aromatic Azoimides.* Part III. *The Naphthylazoimides and their Nitro-derivatives.*" By MARTIN ONSLOW FORSTER and HANS EDUARD FIERZ.

For the purpose of studying further the triazo-group, and the conditions under which its properties are influenced by other groups, azoimides of the naphthalene series have been examined.

α-Naphthylazoimide, $C_{10}H_7 \cdot N_3(\alpha)$, melts at 12°, and does not yield hydrazoic acid when heated with alcoholic potash; the 2-*nitro*- and 4-*nitro*-derivatives, melting at 103—104° and 99° respectively, are resolved into the corresponding nitronaphthols and hydrazoic acid. The heteronucleal 5-*nitro*- and 8-*nitro*-1-*naphthylazoimides*, melting at 121° and 130—131° respectively, do not furnish hydrazoic acid.

β-Naphthylazoimide, $C_{10}H_7{\cdot}N_3(3)$, melts at 33°, and like the heteronucleal *5-nitro-* and *8-nitro-2-naphthylazoimides*, melting at 33·5° and 108° respectively, does not give hydrazoic acid. *1-Nitro-2-naphthylazoimide*, melting at 116—117°, is characterised by the readiness with which it loses nitrogen when heated, passing into the peroxide of β-naphthaquinonedioxime, which is also obtained, but less readily, from the 2-nitro-1-naphthylazoimide; the 1-nitro-2-naphthylazoimide yields hydrazoic acid when heated with alcoholic potash.

*227. "*The Triazo-group.* Part I. *Triazoacetic Acid and Triazoacetone (Acetonylazoimide).*" By Martin Onslow Forster and Hans Eduard Fierz.

The interesting properties displayed by the triazo-group $\begin{matrix}-CH{\cdot}N_3\\ |\\ -CO\end{matrix}$ when occurring in the complex, , have led the authors to prepare the simplest typical compounds of this class, triazoacetic acid and triazoacetone.

Triazoacetic acid, $N_3{\cdot}CH_2{\cdot}CO_2H$, is a colourless substance, which crystallises in lustrous, transparent, hygroscopic plates, melting at 16°; it is a strong acid, has a faint odour recalling that of butyric acid, but much less pungent, and when dropped on a hot iron plate detonates with a moderate explosion, taking fire. The *silver* salt, $C_2H_2O_2N_3Ag$, crystallises from boiling water in lustrous colourless needles, which decompose slowly when exposed to light; the *ethyl* ester, $C_4H_7O_2N_3$, is a limpid colourless oil, which boils at 45° under 2 mm. pressure, and has a very faint odour recalling chloroform rather than ethyl acetate. *Triazoacetamide*, $N_3{\cdot}CH_2{\cdot}CO{\cdot}NH_2$, crystallises from benzene in long lustrous colourless needles, melting at 58°.

The derivatives of triazoacetic acid are much more sluggish in their reaction with concentrated sulphuric acid than is usually the case among compounds containing the triazo-group; when shaken vigorously with the acid, however, nitrogen is liberated. A neutral solution of potassium triazoacetate may be boiled without undergoing change, but in presence of free alkali, two-thirds of the azidic nitrogen is eliminated in the elemental form, the remainder separating as ammonia.

Triazoacetone (acetonylazoimide), $N_3{\cdot}CH_2{\cdot}CO{\cdot}CH_3$, is a colourless limpid oil, which boils at 54° under 2 mm. pressure; the freshly prepared substance has a very faint odour recalling that of chloroacetone, but much less pungent, spontaneously acquiring a suggestion of carbylamine after a few days. It is moderately soluble in water, and when shaken with dilute aqueous potash briskly liberates nitrogen, gas evolution being almost explosive when a 40 per cent solution of alkali is used; dropped on a hot iron plate, the substance detonates feebly, taking fire, and concentrated sulphuric acid decomposes it immediately. The *semicarbazone*, $C_4H_8ON_6$, crystallises from hot water or absolute alcohol in long lustrous needles, which melt without evolving gas at 152°.

The triazo-derivatives of acetone and acetic ester were prepared by the action of sodium azide on the respective chloro-compounds. The authors are engaged in a study of the products obtainable from salts of hydrazoic acid, and the halogen derivatives of acids, esters, ketones, aldehydes, and alcohols.

Discussion.

Dr. Keane asked whether Dr. Forster had examined the decomposition products of the azoimides of acetic acid and ethyl acetate when two-thirds of the total nitrogen was eliminated, and if so, whether imide derivatives of the aldehydes were obtained as in the case of the camphoryl-azoimide?

Dr. Forster replied that these compounds were being investigated.

*228. "*Studies of Dynamic Isomerism.* Part VII. *Note on the Action of Carbonyl Chloride as an Agent for Arresting Isomeric Change.*" By Thomas Martin Lowry and Egbert Hockey Magson.

Labile solutions of nitrocamphor, in which isomeric change has been suspended, have been prepared (1) accidentally by dissolving nitrocamphor in chloroform, and (2) deliberately by adding acid to the solvent chloroform. In the latter case, the solutions acquired a powerful odour of carbonyl chloride, and there can be no doubt that this is the efficient agent in arresting isomeric change in chloroform solutions.

By means of this new agent, it is possible to arrest the isomeric change of nitrocamphor in other solvents. Thus a solution in benzene and N/10,000 carbonyl chloride, when stored in a quartz flask, showed a change of rotatory power of only 1·4° in twenty-five days, whilst a solution to which no carbonyl chloride had been added showed a similar change in four hours. In the same way, the velocity of isomeric change in ether was reduced to one-twentieth by the addition of N/10,000 carbonyl chloride, but no retardation was produced by the addition of acetic anhydride to acetic acid.

*229. "*The Electrometric Determination of the Hydrolysis of Salts.*" By Henry George Denham.

The author has measured the hydrolysis of salt solutions with the hydrogen electrode. The E.M.F. of the cell, Pt_{H_2} | salt solution | saturation sol. of NH_4NO_3 | calomel electrode, was measured, and from this the concentration of the hydrogen ion was calculated.

A redetermination of the hydrolysis of solutions of aniline, chromium, and aluminium salts gave results agreeing well with those obtained by Ley (*Zeit. Phys. Chem.*, 1899, xxx., 193; Bruner, *Ibid.*, 1900, xxxii., 133; Bredig, *Ibid.*, 1894, xiii., 289, and Bjerrum, *Ibid.*, 1907, lix., 336). In the case of the green chromium sulphate, the results obtained point to the conclusion that the equation given by Recoura (*Ann. Chim. Phys.*, 1895, [7], iv., 494) for the conversion of the blue sulphate into the green is not valid, but that the acid formed is produced through hydrolysis, and its amount depends only on the concentration and the temperature of the solution.

In the case of the salts of zinc, magnesium, thorium, cobalt, and nickel, peculiar variations in the hydrogen ion concentrations have been noticed from day to day. The most probable explanation of this appears to be that the hydrolysis of these salts lead to heterogeneous systems, in which the second phase (hydroxide or basic salt) is present in a colloidal form.

230. "*The Interaction of Metallic Sulphates and Caustic Alkalis.*" By Spencer Pickering.

Alkalis, added to solutions of various metallic sulphates, precipitate a definite basic sulphate, except in the case of manganese and magnesium, where the hydroxide is precipitated. After the precipitation is complete, the further addition of alkali converts the basic sulphate either into another, sometimes consecutively into two other, more basic products (for example, copper and nickel), or into the hydroxide (aluminium). When one of the stronger alkalis (potash, soda) is used in excess, the product is probably always the hydroxide, but in the case of lime this does not appear to be so, at any rate not with the sulphates of copper and nickel (see the following communication). In every case examined, different alkalis have given the same results as regards the basicity of the sulphates precipitated by them in each particular case. The existence of the following eleven basic sulphates has been established in this way; the predominance of 5 as the coefficient of equivalents of metallic oxide present is very noticeable. Those marked with an asterisk are the ones formed when the whole of the metal has been precipitated from the solution; the others are products of the action of further quantities of alkali: $5NiO,3SO_3$*, $5NiO,2SO_3$, $5Al_2O_33\times2SO_3$*, $4CuO.SO_3$*, $4CoO,SO_3$*, $4CdO,SO_3$*, $5CuO,SO_3$, $5NiO,SO_3$, $5ZnO,SO_3$*, $10CuO,SO_3$, $10FeO,SO_3$*.

231. "*The Chemistry of Bordeaux Mixture.*" By Spencer Pickering.

The substances formed on the addition of lime to copper

sulphate, as in the preparation of Bordeaux mixture, are dependent on the proportions of lime used, and may be either—

(1) $4CuO,SO_3,0{\cdot}06CaSO_4$;
(2) $5CuO,SO_3,0{\cdot}25CaSO_4$;
(3) $10CuO,SO_3,1{\cdot}3CaSO_4$;
(4) $10CuO,SO_3,4CaO,SO_3$;
(possibly 5) $10CuO,SO_3,10CaO,SO_3$;
or (6) $CuO,3CaO$;

that present in most cases probably being (4).

The fungicidal action of Bordeaux mixture seems to depend on the liberation of normal copper sulphate by the action of carbon dioxide on the basic sulphate. The action begins only after a certain lapse of time, the basic calcium sulphate having to be decomposed before the basic copper sulphate is attacked. By using only sufficient lime to form $4CuO,SO_3$, the presence of basic calcium sulphate and the consequent delay in the action is avoided; in addition to this, the amount of normal copper sulphate liberated (for a given amount of copper sulphate taken) and the insecticidal value of the mixture will be two and a-half times as great as when it consists of $10CuO,SO_3.4CaO,SO_3$.

The basic sulphates, when precipitated by lime in presence of excess of sodium sulphate, contain sodium sulphate as well as calcium sulphate; the formula of the most basic sulphate is $10CuO,SO_4,(Na_2,Ca)SO_4$. When precipitated by soda, they contain no appreciable amount of sodium sulphate, unless a large excess of the latter is present in the liquid.

Nickel sulphate with lime gives a basic sulphate containing a very little calcium sulphate, but, if the lime is at all times in excess, the basic sulphate is deprived of most of its acid, the precipitate consisting essentially of a double oxide.

232. "*The Alcohols of the Hydroaromatic and Terpene Series.* Part I. *Resolution of the Alcohols into their Optically Active Components and the Preparation of the Borneols.*" By ROBERT HOWSON PICKARD and WILLIAM OSWALD LITTLEBURY.

An alternative method to that of the authors' (*Proc.*, 1906, xxii., 71) for the resolution of racemic alcohols was described. The alcohol is combined with phthalic or succinic anhydride, and the resulting acid ester resolved by *l*-menthylamine or other strong optically active base. The optically active acid ester thus obtained is readily hydrolysed and yields the active alcohol in a pure state.

l-Borneol was purified by three independent methods and found to have $[\alpha]_D$ $-37{\cdot}9°$ in toluene solution. *d*-Borneol was obtained from the reduction products of camphor by (i.) treatment with zinc chloride in benzene solution, followed by (ii.) conversion in the hydrogen phthalate and purification by means of the *l*-menthylamine salt. It then has $[\alpha]_D$ $+37{\cdot}8°$ in toluene solution.

*iso*Borneol (from camphene) was converted into the hydrogen phthalate and resolved by means of *l*-menthylamine and cinchonine. The *iso*bornyl hydrogen phthalates have $[\alpha]_D$ $\pm 76{\cdot}8°$ in chloroform solution, and when hydrolysed readily yield the pure *iso*borneols, which have $[\alpha]_D$ $\pm 34{\cdot}3°$ in ethyl-alcoholic solution. The identity of Haller's *iso*camphols (obtained by reduction of camphor), which had $[\alpha]_D$ $\pm 32{\cdot}9°$ in ethyl-alcoholic solution, with the inactive *iso*borneol from camphene has long been assumed. The results described may be taken as proof of this, although it is probable that the product obtained from "camphene" contains other substances beside *d*- and *l*-*iso*borneol.

233. "*The Electrolytic Preparation of Disulphides.* Part I. *Dibenzyldisulphide and Diethyldisulphide.*" By THOMAS SLATER PRICE and DOUGLAS FRANK TWISS.

The electrolysis of the alkyl thiosulphates (compare *Proc.*, 1906, xxii., 260), which are used to prepare the disulphides, was originally performed in a beaker, without any diaphragm between the anode and the cathode, and the formation of disulphides was assumed to be due to the decomposition of the discharged anions, according to the equation $2R{\cdot}S_2O_3 = R_2S_2 + 2SO_3'$.

Subsequent experiments, however, with divided cells, have proved the formation of disulphide to be due to the reduction of the alkyl thiosulphate anion at the cathode, according to the equation $2R{\cdot}S_2O_3' + 2H = R_2S_2 + 2HSO_3'$.

The best yield of disulphide is obtained by using a low current density, a concentrated solution, and current in excess of that theoretically required; the addition of sodium carbonate or bicarbonate to the electrolyte is also advantageous.

Although the pure alkyl thiosulphate compounds were used in the earlier experiments, it has been found quite satisfactory to electrolyse the mixture obtained by heating together sodium thiosulphate and the organic halide in aqueous-alcoholic solution; a divided cell is then used.

The bearing of the above results on the constitution of sodium thiosulphate was discussed, since Gutmann, in a series of recent papers (*Ber.*, 1905, xxxviii., 1728 and 3276, &c.), favours the constitutional formula $\begin{matrix}S\\ O\end{matrix}\!\!\gtrless\!\!S(ONa)_2$ in place of the usually accepted formula $SO_2(ONa)(SNa)$. It was shown that the former formula is not satisfactory, and that all Gutmann's results are in accordance with the latter.

234. "*The Influence of Solvents on the Rotation of Optically Active Compounds.* Part XI. *Ethyl Tartrate in Aliphatic Halogen Derivatives.*" By THOMAS STEWART PATTERSON and DAVID THOMSON.

The rotation of ethyl tartrate has been determined in methylene chloride, carbon tetrachloride, ethylene chloride, ethylidene chloride, acetylene tetrachloride, bromoform, ethyl bromide, ethylene bromide, acetylene tetrabromide, methyl iodide, methylene iodide, and ethyl iodide at various temperatures and concentrations. The values found were compared with those for molecular solution-volume. To some extent an inverse relationship holds between these variables. In all the solvents under consideration, the rotation of the dissolved ethyl tartrate is depressed below that of the homogeneous ester, whilst, on the other hand, the molecular solution-volume becomes greater than the molecular volume. Amongst the individual data also an inverse proportionality often obtains, but a correlation between the two variables cannot be traced through all the solvents examined, since exceptions are both numerous and important.

235. "*The Interaction in Solution of Ferrous Sulphate and Copper Sulphate.*" By HENRY RUSSELL ELLIS and WILLIAM HENRY COLLIER.

When ammonia is added to copper sulphate solution, the distinctive blue colouration is not obtained or is rendered indistinct if ferrous sulphate is present.

If excess of ferrous sulphate is present, no colouration is produced, whilst the iron is precipitated as ferrous and ferric hydroxides; the solution contains cuprous compounds, and a small quantity is present in the precipitate. The production of the ferric hydroxide is brought about by the oxidising action of the compound $CuSO_4,5NH_4OH$, and the amount of oxidation is proportional to the amount of this substance present.

Complete oxidation is brought about when both the copper and ammonia are present in excess.

The authors have been able to oxidise the whole of the iron in a few minutes in the cold by using the proportions $10NH_4OH,CuSO_4$, and $\frac{1}{4}FeSO_4$. Solutions of ferrous sulphate, on boiling, become hydrolysed, giving an acid solution.

No action takes place between ferrous sulphate and copper sulphate solutions in the cold, but, on boiling, the copper sulphate slowly oxidises the ferrous hydroxide produced by hydrolysis.

(To be continued).

SOCIETY OF CHEMICAL INDUSTRY.
London Section.

Ordinary Meeting, December 2nd, 1907.

Mr. R. J. Friswell in the Chair.

"*The Estimation of Naphthalene in Coal-gas and Spent Oxide of Iron.*" By C. J. Dickenson-Gair.

The methods of estimation given in the paper are as follows :—

The Acetic Acid Method.—300 or 400 cc. of acetic acid solution are placed in two Dreschel bottles coupled with a third bottle, containing picric acid solution as a catch. About 10 cubic feet of the coal-gas are passed through, and the contents of the bottles then mixed with 500 cc. strong picric acid solution. On agitating, pure naphthalene picrate separates out, and is filtered. The precipitate is washed with N/40 picric acid solution to free it from acetic acid, and N/10 NaOH is added to it until there is an excess after boiling ten minutes. The reaction is $C_{10}H_8C_6H_2(NO_2)_3OH + NaOH = C_{10}H_8 + C_6H_2(N_2O)_3ONa$. The excess of soda is found by titration while hot, first, with N/20 picric acid and then with N/10 NaOH, using lacmoid indicator. From these data the amount of N/10 NaOH used up in the reaction is found; each cc. = 0·197 grains naphthalene.

The Re-precipitation Method.—The test is commenced in a similar manner to Colman and Smith's, only picric acid solution being used. The mixture of naphthalene and naphthalene picrate is filtered off and transferred to a flask, 50 to 100 cc. absolute alcohol being added. A clear yellow solution results. About 300 cc., concentrated picric acid solution are added, and on agitation pure naphthalene picrate separates out. The same procedure is subsequently followed as in the acetic acid method, only the washing with picric acid is omitted. Experiments proved both methods to be perfectly reliable and very rapid in execution.

A modification of this test is made use of in estimating naphthalene in spent oxide of iron. Ten grms. of the undried oxide are mixed with 100 cc. 80 per cent alcohol. The flask is agitated, allowed to stand several hours, and the liquid filtered. 300 cc. strong picric acid solution are added to the filtrate and washings. On agitation, naphthalene picrate separates out, and is treated as in the re-precipitation method.

"*Note on the Influence of Formal on the Properties of* Funtumia Elastica." By Dr. P. Schidrowitz and F. Kaye.

The authors find that the rubber obtained from the latex treated by formal, although less elastic and resilient than that obtained by other means, was extraordinarily tough. They suggest that a rubber of this character might be particularly suitable for some purposes—*e.g.*, for the covers of motor tyres—where toughness is of relatively greater importance than resiliency, and that it may in the future be found desirable to use different methods of coagulation for the same latex according to the purpose for which the rubber is intended.

"*Polarimetric Determination of Sucrose.*" By Francis Watts and H. A. Tempany.

1. *Effect of Basic Lead Acetate on the Optical Activity of Sugar Solutions.*—In the polarimetric determination of sucrose in raw sugars the most suitable and convenient method of defecation is by means of basic lead acetate. Formerly solutions of the acetate were used, but it was shown that by this means errors of concentration were introduced owing to the space taken up by the precipitate formed. Horne proposed the use of the anhydrous acetate in place of a solution as almost removing this source of error, and the authors in a former paper supported this contention by further experimental work. But some investigators still maintain that there is a serious error in the polarimetric readings caused by the direct action of the basic acetate on the invert and non sugars present. In the present paper it is shown that in ordinary raw sugars if only slight excess of the basic acetate is used the error is so small as to be negligible. If large excess is used the error becomes serious. The error in reading is considered to be due to the basic portion of the lead present, and that if acetic acid is added sufficient to just neutralise the basicity the normal reading is restored. In the determination of molasses, however, the quantities of basic acetate required are so large that the error is considerable, and after partial clarification with anhydrous basic acetate the solution should be mixed with sulphur dioxide, which practically restores the normal rotation.

2. *The Effect of Clarification with Basic Lead Acetate on Cane-juice.*—In raw sugars clarified by basic acetate of lead the primary precipitates contain usually from 50 to 60 per cent of lead oxide, the basic acetate itself containing 81·4 per cent. The clarified liquor almost always contains lead, but still generally gives a further light lemon-yellow coloured precipitate on the addition of more basic acetate. The authors find this precipitate to contain 81 per cent of lead oxide and a very little organic matter which appears to be of a pectinous nature. They believe the lead present in the clarified juice to be due to traces of organic lead salts arising from the neutralisation of the basic lead by organic acids present in the sugars. The influence of these traces of lead salts in the clarified juices on the determination of invert by Fehling solution has been investigated, and it is found that this, though existent, is so slight as to be negligible unless large excess of basic oxide has been used.

"*Niam Fat.*" By Dr. J. Lewkowitsch.

Niam fat was obtained from the seeds of *Lophira alata* (Banks), a tree indigenous to Senegambia, Sierra Leone, and the Egyptian Soudan.

The fat freed from extraneous matter forms 41 per cent of the kernels. It is a soft buttery mass, melting at 24° C., and is used by the natives for culinary purposes and as a hair-oil.

The following characteristics were determined in two specimens :—

	Fat extracted from kernels.	Fat prepared by natives.
Sp. gr. at 40° C. (water at 40° = 1)	0·9105	0·9063
Acid value	18·54	5·78
Saponification value	195·6	190·1
Unsaponifiable matter	1·49	1·38
Iodine value..	68·4	78·72
Mean molecular weight of the fatty acids	—	283·7
Solidifying point of the fatty acids	—	42·5° C.

Iodohydrines and Alkyliodohydrines derived from Styrolene.—Marc Tiffeneau.— When styrolene is subjected to the action of iodine in presence of yellow mercurous oxide in ethereal solution, the iodohydrine, $C_6H_5—CHOH—CH_2I$, is the only product, while in alcoholic solution the alkyliodohydrine $C_6H_5—CHOR—CH_2I$, where R varies according to the alcohol employed, is formed in addition. The oxy-alkyl group is always bound to the carbon atom next the aromatic radical, while the atom of iodine is attached to the carbon furthest from the C_6H_5 group, as may readily be proved in the case of the alkyl iodohydrines by transforming them into *a*-alkyloxystyrolenes, $C_6H_5—CH(OR)—CH_2I \rightarrow C_6H_5C(OR)=CH_2$. The iodohydrine, $C_6H_5—CHOH—CH_2I$, is decomposed as follows by distillation *in vacuo* :—

$$C_6H_5—CH(OH)—CH_2I \rightarrow C_6H_5C(OH)=CH_2 \rightarrow \rightarrow C_6H_5—CO—CH_3,$$

the final product being acetophenone and not phenyl acetic aldehyde. Alcoholic potash transforms this iodohydrine into mono-ethers of phenyl glycol, which are decomposed by sulphuric acid into phenyl acetic aldehyde and not into acetophenone.—*Comptes Rendus*, cxlv., 20,

NOTICES OF BOOKS.

Practical Chemistry. By GEOFFREY MARTIN, B.Sc., Ph.D. London: Crosby Lockwood and Son. 1907.

THIS short course of practical chemistry for army and matriculation candidates, and for use in secondary schools, includes both qualitative and quantitative work. Full directions are given for the preparation of typical gases and salts. The apparatus described is in most cases relatively simple, and the experiments are well chosen for illustrating important reactions and operations. In a book of this type it is difficult to avoid a certain resemblance to a collection of recipes, especially when the author is aiming at sparing the teacher's tutorial work as far as possible; but, on the whole, the student is induced to think for himself, and the exercises and problems upon the work he has done should encourage him to devise simple experiments. The quantitative work includes gravimetric estimations, volumetric analysis, and the determination of solubility, boiling- and melting-points. A chapter on the regulation of work in practical chemistry classes will be appreciated by teachers who find it difficult to estimate and register the progress of their students, and the adoption of the author's suggestions would seem likely to promote a healthy spirit of rivalry in the workers, and to put before them a high ideal of carefulness and accuracy.

The Metric and British Systems of Weights, Measures, and Coinage. By F. MOLLWO PERKIN, Ph.D. London and New York: Whittaker and Co. 1907.

ALTHOUGH the author of this book had more particularly the requirements of science students in his mind when he wrote it, the introduction is addressed more to the great majority of the public who are still unconvinced of the advantages which will follow the universal adoption of the metric system. Dr. Perkin puts his case very clearly and strongly, and gives useful comparisons of well known quantities, which are readily remembered in the metric system, such as the thickness of a sixpence, the width of a stamp, and so on, which will help the student to form a mental picture of the relative magnitude of the English and metric units. For rough calculations the graphs will be found invaluable. There are some worked examples in the book, and the use of the balance and the determination of specific gravity are also described. It seems a pity that the fundamental difference between density and specific gravity is not emphasised for the benefit of the student, even if for general purposes it is thought that such distinctions are unneccessary, and a slip in speaking of a cube of aluminium in centimetres and the weight of a centimetre of water will possibly cause some confusion in the beginner's mind.

Liquid and Gaseous Fuels. By VIVIAN B. LEWES, F.I.C., F.C.S., &c. London: Archibald Constable and Co., Ltd. 1907.

THE author of this book thoroughly understands how to interest the lay reader, and gives a very practical account of the use of liquid and gaseous fuels in power production. The subject is one which in some aspect or other is of considerable moment to a vast section of the general public, and some parts of the book, such as, for instance, those which treat of the calorific value of coal-gas and the heating and illuminating power of oil-lamps, will perhaps help the consumer to form an estimate of the cost and efficiency of various systems of heating and cooking under different conditions. The evolution of the common forms of gas-burners is discussed in some detail, but perhaps the most interesting section of the book is that in which the author forecasts the probable future of the fuel question. He suggests that the peat deposits of the world will shortly be utilised to a much greater extent than they are at present, and believes that when they are exhausted, or even before then, the production of alcohol by fermentation will provide the solution of the problem of the fixation of solar energy.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlv., No. 20, November 11, 1907.

Iodation in Vacuo. — Marcel Guichard. — Ferrous iodide can be prepared by placing iodine and iron separately in a sealed tube which is exhausted by a mercury pump. The part of the tube containing the iron is heated to 500°, and that containing the iodine to 180°. The iodine then vaporises and unites with the iron. Ferrous iodide is dark red in colour. By the same method anhydrous nickel iodide and uranium iodide can also be prepared. In order to prepare iodides which are formed at a high temperature and are very volatile—for example, silicon or aluminium iodide—it is necessary to keep the sealed tube at three different temperatures. All these iodides are formed at pressures lower than atmospheric.

Action of Amorphous Arsenic upon Alkyl Haloids. —V. Auger.—Amorphous arsenic precipitated from a hydrochloric acid solution of arsenious anhydride by stannous chloride or by hypophosphite, is capable of inducing many chemical reactions. Thus, when it is heated in a sealed tube with carbon tetrachloride the hexachloride is formed, $6CCl_4 + 2As = 2AsCl_3 + 3C_2Cl_6$. With chloroform amorphous carbon is formed: $3CHCl_3 + 2As = 2AsCl_3 + 3HCl + 3C$. Iodoform and amorphous arsenic react with an explosion when heated together on the water-bath. If a neutral solvent, such as benzene or toluene, is employed the action proceeds quietly, and the study of the reaction shows that it occurs quantitatively according to the equation $3CHI_3 + 2As = (CHI_2)AsI_2 + (CHI_2)_2AsI$. Nitric acid with these iodides gives the corresponding acids:—

$$(CHI_2)AsI_2 + 4HNO_3 = (CHI_2)As{<}^{O}_{OH}{}_{OH} + 4NO_2 + H_2O \text{ and}$$

$$(CHI_2)_2AsI + 3HNO_3 = (CHI_2)_2As{=}O{<}_{OH} + 3NO_2 + H_2O.$$ Di-iodomethyl arsenic acid crystallises in yellow tablets with one molecule of water. Warm aqueous solutions of alkalis decompose it quantitatively as follows:— $(CHI_2)AsO_3H_2 + 2NaOH = CH_2I_2 + AsO_4HNa_2 + H_2O$. Tetra-iodo cacodylic acid with soda gives methylene iodide and arsenate.

Action of Urea, Thiourea, and Urethane, and some Amides on Xanthone Hydrol.—R. Fosse.—With a certain number of primary amides xanthone hydrol gives one molecule of water and a monamido monoxanthane compound. With unsubstituted diamides, such as urea or thiourea, the reaction is similar, one molecule of the diamine combining with two of the xanthone hydrol,—

$$O{<}^{C_6H_4}_{C_6H_4}{>}CHOH + HNH{>}CO = O{<}^{C_6H_4}_{C_6H_4}{>}CHOH + HNH{>}CO =$$

$$= H_2O + \left[O{<}^{C_6H_4}_{C_6H_4}{>}CH\right]_2 NH{>}CO.$$

One molecule of xanthone hydrol reacts with sulpho-urea, giving phenyl monoxanthyl sulpho-ureas. The xanthones monamides and dixanthone diamides react with acids as follows :—

$$\left[O<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>CH\right][NH.CO.R] + HCl =$$

$$= NH_2COR + CH<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>OCl.$$

$$\left[\begin{matrix}O<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>CH\\O<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>CH\end{matrix}\right]\begin{matrix}NH\\NH\end{matrix}\Big\rangle CO + 2HCl =$$

$$\begin{matrix}NH_2\\NH_2\end{matrix}\Big\rangle CO + 2CH<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>OCl.$$

Application of Hofmann's Reaction to Sparteïne.—Charles Moureu and Amand Valeur.—The products obtained by applying Hofmann's reaction to the hydrate of α-methyl sparteïne are :—Methyl sparteïne, $C_{15}H_{25}N_2CH_3$; dimethyl sparteïne, $C_{15}H_{24}N_2(CH_3)_2$; and, finally, hemisparteïlene, $C_{15}H_{23}N$. These all behave like mixtures, and the authors have not attempted to extract definite products from them. Raw methyl sparteïne, when subjected to the action of methyl iodide, is only 66 per cent methylated, and when the non-methylated part is separated off a raw dimethyl sparteïn is obtained. With excess of methyl iodide this gives di-iodomethylate, converted by silver oxide into the dihydrate of tetramethyl sparteïne, the decomposition of which gives methyl hemisparteïlene, $C_{16}H_{25}N$.

Determination of Fat in Skim Milk.—R. Lezé.—The fat remaining in skim milk can be very rapidly determined as follows :—A solution of caustic soda, 20 grms. in 150 to 180 cc. of ammonia, is made up to 250 cc. To 3 litres of the milk heated to 40°, 6c cc. of this reagent are added, and the milk is then skimmed again in a separator. It is found that all the fat is concentrated in the cream, which can then be analysed by any of the usual methods.

MISCELLANEOUS.

Royal Institution.—*Friday Evening Meetings before Easter*, 1908 :—

January 17, Prof. T. E. Thorpe, C.B., Ph.D., LL.D., D.Sc., F.R.S., M.R.I., "The Centenary of Davy's Discovery of the Metals of the Alkalis."
January 24, Colonel David Bruce, R.A.M.C., C.B., D.Sc., F.R.S., "The Extinction of Malta Fever."
January 31, Prof. Ernest Rutherford, M.A., LL.D., D.Sc., F.R.S., "Recent Researches on Radio-activity."
February 7, Humphry Ward, Esq., M.A., "Napoleon and the Louvre."
February 14, Caleb Williams Saleeby, Esq., M.D., F.R.S.E., "Biology and History."
February 21, Sir Oliver Lodge, LL.D., D.Sc., F.R.S., M.R.I., "The Ether of Space."
February 28, Prof. William Arthur Bone, D.Sc., Ph.D., F.R.S., "Explosive Combustion, with Special Reference to that of Hydrocarbons."
March 6, Prof. John Milne, D.C.L., D.Sc., F.R.S., F.G.S., "Recent Earthquakes."
March 13 (Vacant).
March 20, Prof. A. E. H. Love, M.A., D.Sc., F.R.S., "The Figure and Constitution of the Earth."
March 27, Hon. Robert John Strutt, M.A., F.R.S., "Radio-active Change in the Earth."
April 3, The Rt. Hon. Lord Montagu of Beaulieu, D.L., V.D., J.P., &c., Vice-Ptesident, Royal Automobile Club, Editor of the *Car*, "The Modern Motor-car."
April 10, Prof. Joseph Thomson, M.A., LL.D., D.Sc., F.R.S., M.R.I., "The Carriers of Positive Electricity."

MEETINGS FOR THE WEEK.

MONDAY, 16th.—Society of Arts, 8. (Cantor Lectures). "Theory of the Microscope," by Conrad Beck, F.R.M.S.
TUESDAY, 17th.—Society of Arts, 8. "How to Make the Most of a Museum," by Lewis Foreman Day.
WEDNESDAY, 18th.—Microscopical, 8. "Some African Rotifers," by J. Murray. "Gregory and Wright's Microscope" and "A Correction for a Spectroscope," by E. M. Nelson. Exhibition of Selenite Specimens, showing interesting Features due to Twinning, by E. Large.
—— Society of Arts, 8. "The *rôle* of France in West Africa," by Mons. Lucien Hubert, Député des Ardennes. (The author will read his paper in French).
THURSDAY, 19th.—Chemical, 8.30. "Derivatives of Tetramethyl Glucose," by J. C. Irvine and A. M. Moodie. "Characterisation of Mercerised Cotton," by J. Hübner. "Attempted Synthesis of β—N—β / β—CH—β dinaphthacridine—Condensation of Methylene Dichloride and 1-Substituted-2-naphthylamines," by A. Senier and P. C. Austin.

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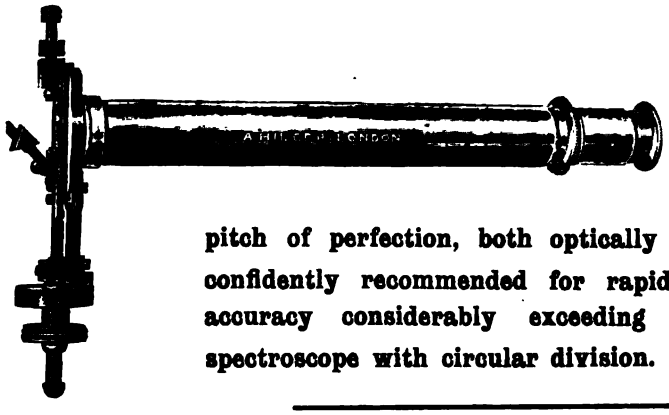

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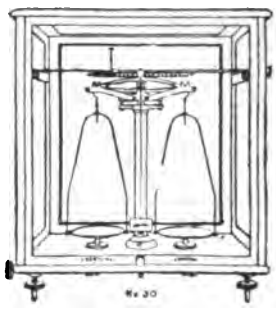

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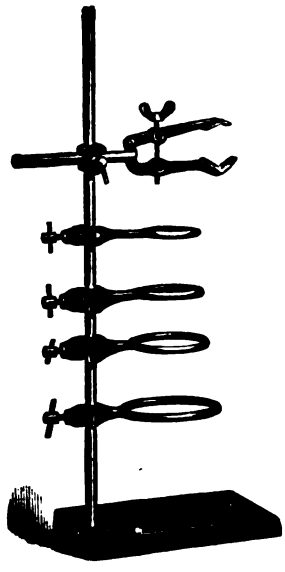

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THE ORIGIN OF COLOUR IN ORGANIC COMPOUNDS.

By PERCY MAY.

(Concluded from p. 285).

Part II.

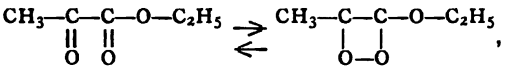
So long as attention was paid only to whether a substance was coloured or not, little progress could be made as the subject was necessarily of a qualitative and empirical nature. The application of spectroscopy has brought a new and searching light to bear upon the problem of colour, and has furnished the quantitative basis necessary to raise the study of the origin of colour to the level of an exact science.

Hartley was the chief pioneer in the study of the ultra-violet absorption spectra of organic compounds, and he has discovered certain most important facts connecting chemical constitution and absorption spectra. The method employed by Hartley was to measure the absorption limits at a great many concentrations, always gradually increasing the dilution until complete transmission was obtained. The oscillation frequencies of the edges of the regions of absorption were then plotted against the corresponding strengths of solution, and a curve drawn through the points so obtained. It is the shape of these curves that has been connected with the chemical constitution of the substances.

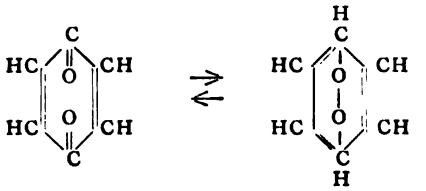
Recently much work has been done in this direction by Baly and others, and they have employed a slightly different form of plotting the results. Hartley, in his later work, plots equivalent thickness of solution instead of strength of solution, while Baly and his co-workers have plotted the logarithms of the relative thickness instead of the values themselves. This method has the great advantage that a given relative change of concentration is represented by the same change of ordinates in any part of the diagram. In his investigation of the spectrum of benzene, Hartley discovered six absorption bands close together, but later Baly and Collie found seven (*Trans. Chem. Soc.*, 1905, lxxxvii., 1332). Now, in the vibration of the benzene molecule, as described by Collie (*Trans. Chem. Soc.*, 1897, lxxi., 1013), there are seven possible changes of linkage between the carbon atoms, and therefore it seemed highly probable that the actual linkage change is the cause of the absorption band. This, for the first time, actually indicates a physical cause of colour, and subsequently Baly and Desch, from their investigation of acetyl acetone, $CH_3.CO.CH_2.CO.CH_3$, obtained results in accordance with this view. They found that the absorption was the same if the hydrogen were replaced by beryllium, sodium, or even the very heavy thorium. They therefore concluded that the absorption was not due to the vibration of the atom itself (H, Be, Na, or Th) but to the actual change of linkage, $CH_2—CO— \rightleftarrows —CH=COH$, in the molecule brought about by enol-keto tautomerism, $CH_3.CO.CH_2.CO.CH_3 \rightleftarrows CH_3—CO.CH=C(OH)—CH_3$, and this was confirmed by the fact that neither the pure ketonic nor the pure enolic form of aliphatic tautomeric substances gave an absorption band.

Subsequently, Baly and Stewart investigated the spectra of substances containing the carbonyl group, such as ketones and quinones, and from the results obtained they concluded that the reactivity of any carbonyl group is not inherent in the group itself, but is produced by the reaction of neighbouring atoms. It is supposed that such action may take the form of tautomerism, or of a modification of tautomerism, in which there is no actual transfer of a hydrogen atom, but some inter-atomic disturbance in the grouping $—CH_2—CO—$.

It was found from a study of substances containing two carbonyl groups in the *a*-position to one another, that in those cases the position of the absorption band was shifted towards the red, with the production therefore of colour. As an example, pyruvic ester has an absorption band of great persistence at a frequency of 2070. In this case, the inter-atomic disturbance can be represented, as—



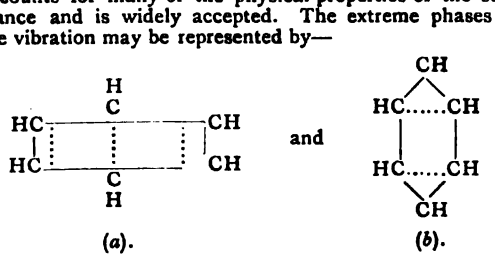
and Baly and Stewart propose the term isorropesis to denote this finer play of forces between two carbonyl groups. The theory of isorropesis will give an explanation of the cause of colour in quinonoid bodies, for isorropesis can occur between the residual affinities of the oxygen atoms, which results in the absorption of light in the visible region of the spectrum. It has not been possible to



give more than a sketch of the theory of isorropesis, but a clear account of it is given by Baly and Stewart in the *Astrophysical Journal*, Sept., 1906, xxiv., p. 100, and in the *Transactions of the Chemical Society*. These results are not antagonistic to the ordinary theory of quinonoid structure, but, on the contrary, they supply the key to it, and indicate *why* quinonoid bodies should be coloured.

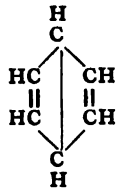
In considering the colour of diphenylfulvene and of diphenylquinomethane, attention was drawn to the fact that the colour was more pronounced in the case of a molecule containing ethylenic double bonds than in one in which these double bonds have been replaced by an aromatic ring. In the former case there is, according to modern views, a far greater residual affinity, and it is the presence of this residual affinity that causes inter-atomic disturbances and isorropesis, and therefore colour.

It has been previously stated that the ordinary theories do not offer any explanation of the colour of compounds, such as meta-nitraniline, but by a consideration of the modern views of the constitution of benzene, Baly, Edwards, and Stewart have ingeniously extended the theory of isorropesis to include meta-quinones. They found that the three nitranilines and the three nitrophenols in alkaline solution give absorption spectra which indicate the existence of a quinonoid form, and the process of isorropesis as the origin of colour. It is therefore necessary to assume the transitory existence of a meta-quinone, and this is possible if the benzene molecule be regarded as undergoing the same vibrations as are suffered by an elastic ring. This vibration theory of the benzene molecule accounts for many of the physical properties of the substance and is widely accepted. The extreme phases of the vibration may be represented by—



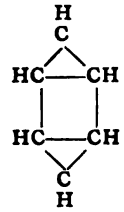
(*a*). and (*b*).

or using the ordinary hexagon formula, these same two extreme phases between which the molecule is pulsating are :—



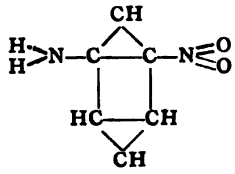
(*a'*).

and

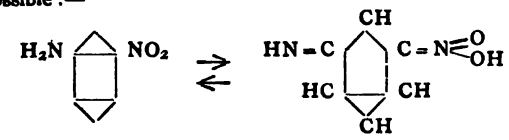


(*b'*).

The ordinary formula for meta-nitraniline in phase (*b*) is—

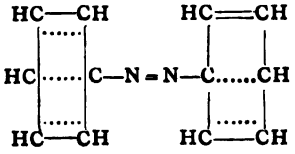


but in this phase isorropesis involving a meta-quinone is possible :—

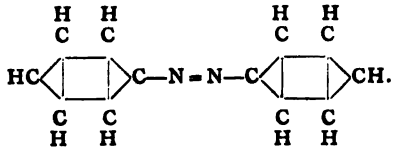


This conception of the meta-quinone is, of course, of very great value, as it can be applied to many compounds of which the colour cannot be explained by the older theories.

The elastic ring theory of benzene is also made use of by Baly and Tuck to account for the colour of the azo-compounds. Thus azo-benzene, $C_6H_5—N=N—C_6H_5$, will exist in the extreme phases—

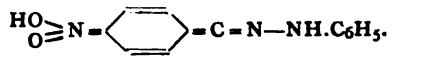


and—

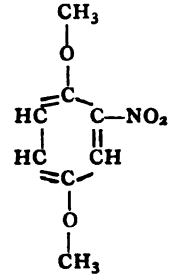


In the second phase, the C atoms, which are united to the N, are unsaturated, and therefore isorropesis can occur between them and the N atoms. This view is in harmony with the fact that $C_6H_5—N=N—CH_3$ is far less coloured than $C_6H_5—N=N—C_6H_5$, and similarly when the C_6H_5 is replaced by any alkyl group. When exposed to light the hydrazones of the aldehydes become yellow, and Baly and Tuck (*Trans. Chem. Soc.*, 1906, lxxxix., 983) have obtained very complete evidence to show that the compound so formed is an azo-compound, the colour of which is, of course, explainable on the above hypothesis.

The actual hydrazones of the nitrobenzaldehydes are brilliant yellow, and in this case the spectra are quite similar to those of the nitrophenols and totally different from those of the azo-compounds, and it therefore appears that they, like the nitrophenols, exist in the quinonoid form :—



Until very recently, the theory of isorropesis was able to account for practically every case of colour due to the linkage of the atoms, but, now some facts have been brought to light which cannot be explained by its aid, and necessitate a new development of the subject. Thus, nitrodimethylquinol,—



is said to be bright yellow, and its colour cannot be accounted for by any existing theory. Much therefore still remains to be done, but there can be no doubt that spectroscopic methods have thrown much light on chemical constitution where purely chemical methods have failed. Certainly, a study of colour theories, past and present, will convince one of the truth of Hartley's statement, that "by the systematic study of absorption spectra can we alone obtain the necessary accumulation of facts which may enable us to arrive at a just conclusion as to the origin of colour."

THE

EFFECT OF HEATING YELLOW PHOSPHORUS IN AMMONIA GAS.

By WILLIAM G. LLEWELLYN.

ALTHOUGH the action of ammonia on compounds of phosphorus is well known, the action of the gas on the element (yellow and red) does not appear to have attracted much attention.

It was thought that excess of ammonia might give either the amines $P(NH_2)_3$ and $P(NH_2)_5$, and phosphine, or perhaps the nitride P_3N_2, and phosphine.

The result of an investigation of the point shows that between the temperature 10° C. and 290° C. (*i.e.*, the boiling-point of phosphorus) there is no action. The results are, however, interesting.

A Würtz flask fitted with an inlet tube reaching nearly to the bottom of it. A thin small flask fitted to the stem acted as receiver, and was cooled by a current of cold water. The outlet tube from the receiver was placed in one of the holes at the bottom of a Bunsen burner, that any phosphine from reactions might be decomposed and the excess of ammonia gas also destroyed. The ammonia was prepared from the aqueous solution by warming, and dried by passing up one tower of quick-lime. The flask was also fitted with a T-tube so that the current of gas could be easily stopped if necessary.

Ammonia was passed through the apparatus for fifteen minutes to expel all the air. A piece of phosphorus, freshly cut so as to expose a clean surface, and dried, was then introduced into the flask. Ammonia gas was passing all the time. No action resulted even on gently heating the flask until the phosphorus melted. On heating the phosphorus to its boiling-point it was found that a white substance condensed on the cooler parts of the flask, and

afterwards clear colourless globules also condensed in the stem. By warming this part of the apparatus the substance was partly driven over into the receiver. During this time the end of the exit tube was dipping into ammoniacal copper sulphate solution, but no copper phosphide was formed, therefore no phosphine had been produced. The whole of the phosphorus had been distilled, none remaining in the Würtz flask. The apparatus was cooled and the distillate examined.

On admitting air to the small flask the white substance was found to glow, and gave off white fumes, indicating unchanged phosphorus. The clear colourless globules in the stem of the flask were examined and found to be solid. The melting-point corresponded with that of ordinary phosphorus. On standing in air so that superficial oxidation might begin, the phosphorus became yellow, like ordinary yellow phosphorus. On warming with water it gradually returns to the ordinary modification. It was found to be soluble in carbon bisulphide.

Remsen and Keiser (CHEMICAL NEWS, xlviii., 201) obtained white phosphorus by distilling yellow phosphorus in a current of purified hydrogen. The method now described is probably simpler and is not dangerous, as no free hydrogen is present to cause the explosive mixture which they state is liable to be obtained in the final operation of their method. No special purification of the ammonia gas is necessary either.

Ammonia gas passed over red phosphorus between 10° C. and 100° C. has no apparent action, the phosphorus remaining unchanged.

Conclusion.—White phosphorus may be obtained by distilling yellow phosphorus in a current of ammonia gas.

The Polytechnic, Regent Street, London.

A METHOD FOR THE DETECTION OF COCOANUT OIL IN BUTTER FAT.

By T. R. HODGSON, B.A., A.I.C.

THIS research was not undertaken with a view to increasing the already voluminous literature on this subject, but with a view to obtaining some method which is short and easily workable in a practical laboratory, and which at the same time enables the sophistication of butter fat with cocoanut-oil to be detected with certainty.

The author has shown (CHEMICAL NEWS, 1907, xcv., 121) that the methods at present in use for the detection and estimation of cocoanut oil in butter fat are more or less useless.

At the present time butter may be unblushingly placed on the market which is known to be adulterated with this oil, and, owing to the present state of the law, it is almost impossible to detect this fraud, for the adulteration is carried on so scientifically that the constants of the mixture are kept within the range of the constants which are usually taken to be consistent with pure butter.

The method followed in this paper is that described in the two previous papers for the determination of the "oxygen equivalent," but it would perhaps be as well to give the method again.

One grm. of the filtered fat is weighed out into a flask, and 25 cc. of a half normal alcoholic solution of caustic potash are added; the flask is then attached to a reflux condenser, and the whole is heated on a boiling water-bath for thirty minutes.

After the saponification is complete, the flask is detached from the condenser, and the solution is evaporated to dryness on the water-bath; 50 cc. of distilled water are then added, and the whole evaporated again to dryness; this operation is continued until the whole of the alcohol has been driven off.

After the whole of the alcohol has been driven off, the residue is dissolved in water and made up to 1000 cc.; 20 cc. of this solution are measured out into a beaker, and 50 cc. of a tenth-normal solution of potassium permanganate, and 50 cc. of a roughly 50 per cent solution of sulphuric acid are added; the beaker is then placed on a boiling water-bath for half-an-hour, and the excess of potassium permanganate titrated with a standard solution of ferrous ammonium sulphate.

The number of cc. of potassium permanganate solution used multiplied by 4 gives the "oxygen equivalent" or the number of grms. of oxygen required to oxidise 100 grms. of the oil or fat. The numbers obtained with mixture of butter fat and cocoanut oil were as follows:—

Sample.	Cc. of $K_2Mn_2O_8$ used.	Difference.
A.	41·8	
		1·6
B.	40·2	
		2·2
C.	38·0	
		2·4
D.	35·6	
		1·6
E.	34·0	
		2·2
F.	31·8	
		2·2
G.	29·6	
		2·0
H.	27·6	
		1·8
M.	25·8	
		2·0
P.	23·8	
		2·0
Q.	21·8	

Even a cursory glance at the numbers given above will show that the difference, though not quite so, is very nearly constant; the average difference between any two samples is 2·0, and it will be seen that no two samples differ more than 0·4 of a cc. from the average.

Sample.	"Oxygen equivalent."	Cocoanut oil (per cent). Calculated.	Actual.
A.	167·2	—	—
B.	160·8	8	10
C.	152·0	19	20
D.	142·4	31	30
E.	136·0	39	40
F.	127·2	50	50
G.	118·4	59·7	60
H.	110·4	71·0	70
M.	103·2	80	80
P.	95·2	90	90
Q.	87·2	—	100

The Sample A was pure butter fat and the Sample Q pure cocoanut oil.

In three cases the calculated percentage of cocoanut oil agrees exactly with the actual percentage, in two cases the calculated percentage is in excess of the actual, and in the other four cases the calculated percentage is slightly less than the actual.

The author hopes that the method described in this and the two preceding papers will be found to be of use in the detection of this the most disgraceful form of adulteration, or that it may form a foundation on which may be built in the future a superstructure sufficiently strong to obtain the desired object.

Analytical Department,
University of Birmingham.

Lupeol.—P. van Romburgh.—When lupeol is boiled with acetic anhydride in presence of sodium acetate a product is obtained which boils at 212—213°, and which causes a considerable lowering of the melting-point of lupeol. Its analysis shows that it is an acetate. When lupeol is obtained from "bresk" it behaves quite differently under the action of these reagents, which led the author to investigate the effect of heat upon it. When it is heated in a glass boat in an exhausted tube furnished with a reservoir containing sulphuric acid a sublimate is found in the tube. There is no loss of water on heating to 190°, and hence it must be concluded that the substance is converted into another modification.—*Comptes Rendus*, cxlv., No. 22.

THE NITROSO-β-NAPHTHOL METHOD FOR THE QUALITATIVE SEPARATION OF NICKEL AND COBALT.

By WILLIAM H. CHAPIN.

The nitroso-β-naphthol method for the qualitative separation of nickel and cobalt is not a new one; and, in view of what has already been written on the subject, anything further may seem superfluous. However, this paper has two excuses to offer for its existence.

1. For the sake of those who are unacquainted with the method, it will aim to make the directions for the cobalt test more explicit than those usually given.

2. It will present a method for determination of the nickel, which so far as the author knows is new.

The things this paper contains may be familiar to many; but for the sake of benefitting those who are still wandering in the dark, I shall brave the fear of repetition, and give them out for what they are worth.

Cobalt.

Beginning at the point where the nickel and cobalt exist alone as sulphides after removal of zinc and manganese, we proceed as follows:—

Place paper and contents in a casserole, add 10 cc. dilute hydrochloric acid (1 : 4) and 1 cc. dilute nitric acid (1 : 3) and boil until only the paper and separated sulphur remain undissolved. Now filter, washing the paper slightly, return the filtrate to the casserole, and boil down to complete dryness, taking care to remove the casserole from the flame a little before this point is reached, so as not to overheat and render the residue insoluble. Take up with two or three drops of dilute hydrochloric acid and 10 cc. hot water, and add a solution of nitroso-β-naphthol in slight excess. The cobalt comes down as a very bulky brick-red precipitate of cobalti-nitroso-β-naphthol, $Co(C_{10}H_6ONO)_3$. After stirring and allowing to stand a few minutes, filter, and confirm the presence of cobalt by means of the borax head. Before testing for nickel, add a few drops more nitroso-β-naphthol to the filtrate to make sure that the cobalt is all removed, and of course filter off any precipitate that may be formed.

Notes.

Hydrochloric acid in large quantities and nitric acid even in small quantities interfere with the precipitation of cobalt; hence the evaporation.

The solution of nitroso-β-naphthol is made up as follows:—Weigh out 8 grms. of the solid reagent, dissolve in 300 cc. cold glacial acetic acid, dilute with an equal volume of water, and filter. In this way is obtained a saturated solution in 50 per cent acetic acid. For best results, the reagent should be made up as often as once a month, as it does not keep very well.

Owing to the bulkiness of the cobalt precipitate, we usually make up our unknowns with only a small amount of cobalt present (2 grms. crystallised cobalt nitrate per litre). Giving out about 5 cc. of such a solution in an unknown, only about 3 cc. nitroso-β-naphthol solution will be required for complete precipitation. It is, however, by no means necessary to limit the quantity of the cobalt.

The test for cobalt, as above stated, has always given perfectly satisfactory results even with beginners, good tests for cobalt being obtained with certainty, when the quantity present was less than a milligrm. Indeed, we have had difficulty in obtaining nickel salts of such purity that our students would not obtain a test for cobalt even when we did not intend it to be present.

Nickel.

The main difficulty we have experienced with the method has rested with the test for nickel. In their usual form the directions for this test read as follows:—"Make the filtrate from cobalt alkaline with ammonium hydroxide, filter off the precipitated nitroso-β-naphthol, and pass hydrogen sulphide. Confirm the presence of nickel by means of the borax bead."

So far as our experience goes, the test in this form has always been a failure. With our classes failure became so common that the students lost all confidence in the method, and reported largely at random. We even made up our unknowns so that the amount of nickel exceeded that of cobalt ten to one (which only showed the weakness of the method and in no wise overcame it), and even then the number of failures was scarcely less. However, considering the shortness and simplicity of the method and its accuracy for the detection of cobalt, we determined not to give it up without some attempt at making it what it promised to be.

Thinking that possibly the nickel might be lost during the washing of the sulphides, as a result of oxidation and consequent solution, we investigated and found that the loss of nickel from this cause was not worse than the loss of cobalt, which amounted to very little.

Next, we tested the solubility of nickel sulphide in the cold dilute (1 : 10) hydrochloric acid used to dissolve out zinc and manganese, but here again the loss was found to be very small.

At last we turned our attention to the final filtrate in which hydrogen sulphide had failed to give a precipitate of nickel sulphide when nickel salts were known to be present in the original solution. We thought that perhaps the organic matter left in the solution was preventing the precipitation, but were surprised to find that this filtrate contained no nickel. The cause of the difficulty was now plain: In making the solution alkaline, and filtering off the precipitate of nitroso-β-naphthol, we were removing from the solution large quantities of nickel, the amount removed depending upon the excess of nitroso β-naphthol.

What we needed, then, was a method by which we could remove the nitroso β-naphthol, so that the solution might be made alkaline for precipitation of nickel without removing the nickel. The method most easily worked out seemed to be the common one for removal of organic matter, viz., oxidation by means of sulphuric and nitric acids. Trial proved the method to be quick, easy, and always successful. Best of all, it did not interfere in any way with the subsequent test for nickel.

The details of this process as we apply it and of the final test for nickel are as follows:—

To the filtrate from cobalt add 5 cc. of dilute sulphuric acid (1 : 5) and 1 cc. of nitric acid (1 : 3), and boil down in a casserole until dense white fumes of sulphur trioxide are evolved. If a dark colour still remains, cool somewhat, add two or three drops more of nitric acid, and again heat until fumes of sulphur trioxide appear. By this time all organic matter should be removed and the solution should be coloured only yellow at most. Cool now completely, cautiously add 5 cc. water and a piece of litmus-paper, and then drop in ammonium hydroxide with constant stirring until the paper is distinctly blue, but avoiding an excess. Now remove the paper, transfer the solution to a test-tube, and pass hydrogen sulphide. A black precipitate is probably nickel. Confirm by means of the borax bead.

Note.

If through careless work the cobalt is not all removed in its proper place, the excess will appear with the nickel; or, if no nickel is present, in place of the nickel. However, we have never seen enough cobalt carried over to obscure the bead test for nickel, where that element was present; and, on the other hand, in absence of nickel, the bead test never fails to disclose the identity of the small amount of cobalt sometimes carried over. If the work is carefully done, no cobalt will ever be carried over, as its removal by this process is quantitative.

We have been using this method for the nickel determination long enough to discover the weak points, if there

were any, and are perfectly satisfied with the results. Failure on the part of our students is a very rare thing, although we have greatly cut down the amount of nickel in our unknowns. I think we are safe in saying that the test for nickel is fully as delicate as that for cobalt; and the ease and rapidity with which it is carried out make it the best method, in our estimation, we have ever used.—*Journal of the American Chemical Society*, xxix., No. 7.

THE DETERMINATION OF CHLORIDES OR BROMIDES IN THE PRESENCE OF SULPHOCYANATES.*

By M. A. ROSANOFF and ARTHUR E. HILL.

1. *Introductory*

IN the course of a research undertaken in the Havemeyer Chemical Laboratory, New York University, it became necessary to analyse a number of solutions containing mixtures of chlorides and sulphocyanates. Investigation of the literature of the subject showed that no method exists by which such mixtures can be analysed quickly and accurately; it was found that those methods which can be relied upon for accuracy of results require such expenditure of time as prohibits their use where large numbers of analyses must be performed. In like manner search revealed no suitable method for the analysis of bromide-sulphocyanate mixtures.

To remedy this lack, the following volumetric method is proposed. It permits of an accuracy within the limits of the usual errors of measurement with pipettes and burettes, and requires less time than any of the existing methods; a single complete determination has been found to require about one and one-half hours, while two determinations can be performed without difficulty in two hours. By proper organisation of the work eight to ten analyses can easily be made within a working day.

The sum of chloride and sulphocyanate, or of bromide and sulphocyanate, is established by precipitation with excess of standardised silver nitrate and determination of the excess by titration with standardised ammonium sulphocyanate, according to the method of Volhard (*Journ. Prakt. Chem.*, 1874, ix., 217; *Zeit. Anal. Chem.*, 1874, xiii., 171). Precipitates containing silver chloride must be filtered off before the excess of silver nitrate is determined, while in the case of the bromide filtration is unnecessary (Rosanoff and Hill, *Journ. Am. Chem. Soc.*, 1907, xxix., 269; CHEMICAL NEWS, xcvi., 264; *Chem. Centr.*, 1907, i., 1596). The new method has for its object the determination of the chloride or bromide in a fresh sample of the solution, by oxidising the sulphocyanate to hydrocyanic acid by means of nitric acid, expelling nearly all the hydrocyanic acid, and determining the residual chloride or bromide, in the presence of the traces of cyanide, by the Volhard method. The sulphocyanate originally present is found by difference.

2. *Determination of Chlorides.*

The following solutions are required:—(*a*) A fifteenth-normal solution of silver nitrate, standardised gravimetrically or by weight of silver nitrate used; (*b*) a fifteenth-normal solution of ammonium sulphocyanate, standardised against the silver nitrate by Volhard's method; (*c*) a saturated solution of iron-ammonium alum, free from chlorides, and treated with nitric acid to lighten the colour.

A measured volume of the chloride-sulphocyanate mixture is diluted so that the normality of the chloride is about one-fiftieth. The solution is treated with 1 cc. of the iron-ammonium alum, and brought to a boil in a large Erlenmeyer flask. To the gently boiling solution concentrated nitric acid is added at the rate of about three drops a minute, during which operation the liquid should be frequently stirred to prevent superebullition. The addition of the acid in the above described manner is continued until the colour of the solution has faded to a *pale orange*, and then without further addition of acid the solution is allowed to boil for a few minutes longer, by which treatment the last traces of sulphocyanate are oxidised. The complete oxidation requires about twenty minutes time; a change of colour to pure yellow indicates the completion of the operation. The odour of hydrocyanic acid is now practically gone.

Cool the solution thoroughly under the tap, and add to it one-third its volume of concentrated nitric acid. Add a measured amount of N/15 silver nitrate in moderate excess above the quantity required to precipitate the chloride, and shake the mixture until the precipitate is well coagulated, which requires but a few minutes' agitation when the solution is cool, but *a much longer time if the solution is heated.* When the precipitate is well coagulated bring the solution again to a gentle boil, maintaining it at this temperature for about five minutes. The liquid above the precipitate must become perfectly clear.

Filter the solution while still hot through a rapid-running double filter, paying no attention to the opalescence which forms in the filtrate upon cooling. Wash the precipitate with hot water containing a few drops of nitric acid. Allow the liquid to cool thoroughly, dilute until the volume is about three times that of the solution before filtration, add 2 cc. of the iron indicator for every 100 cc. of solution, and run in the standardised sulphocyanate to a strong red colour. Stir the solution for five minutes, and then add the standardised silver nitrate drop by drop, with stirring, until the colour just disappears. A single drop of the sulphocyanate solution should then give a permanent pink colour; should it fail to do so, titrate back and forth with the silver nitrate and ammonium sulphocyanate until the colour changes on addition of a single drop. The titration is best conducted in a porcelain dish, against the white ground of which the end-point is most accurately determined; in glassware transmitted light effects may be misleading. The total silver nitrate added, *minus* the total ammonium sulphocyanate added, is the silver nitrate equivalent of the chloride present.

The following is a list of ten consecutive analyses of mixtures of potassium chloride and sulphocyanate performed according to the foregoing directions:—

	N/15 KCl solution.	N/15 KCNS solution.	$AgNO_3$ equivalent of KCl taken.	$AgNO_3$ equivalent found.	Absolute error.
	Cc.	Cc.			Cc.
1.	0·00	25·00	0·00	0·02	+0·02
2.	10·00	90·00	9·95	9·96	+0·01
3.	25·00	50·00	24·87	24·87	0·00
4.	25·00	50·00	24·87	24·86	−0·01
5.	25·00	25·00	24·87	24·88	+0·01
6.	25·00	25·00	24·87	24·93	+0·06
7.	25·00	10·00	24·87	24·83	−0·04
8.	25·00	5·00	24·87	24·90	+0·03
9.	25·00	3·00	24·87	24·84	−0·03
10.	25·00	0·15	24·87	24·90	+0·03

3. *Determination of Bromides.*

The analysis of bromide-sulphocyanate mixtures is conducted precisely as that of the chloride mixtures, with three modifications:—(*a*) the solution to be treated with nitric acid for the destruction of the sulphocyanates should be diluted to roughly one-hundredth normality with respect to bromides; (*b*) after the sulphocyanate has been decomposed at the boiling temperature and the liquid thoroughly cooled, only one-sixth its volume of concentrated nitric acid is added; (*c*) the precipitated silver salts should not be filtered off before the excess silver nitrate is determined.

* Presented before the New York Section of the American Chemical Society, May 10, 1907. From the *Journal of the American Chemical Society*, xxix., No. 10.

The following analyses of bromide-sulphocyanate mixtures were made according to the above directions :—

	N/15 KBr solution. Cc.	N/15 KCNS solution. Cc.	$AgNO_3$ equivalent of KBr taken.	$AgNO_3$ equivalent found.	Absolute error. Cc.
1.	25·00	0·15	22·72	22·76	+0·04
2.	25·00	0·15	22·72	22·69	−0·03
3.	25·00	3·00	22·72	22·73	+0·01
4.	25·00	5·00	22·72	22·78	+0·06
5.	25·00	10·00	22·72	22·69	−0·03
6.	25·00	10·00	22·72	22·68	−0·04
7.	25·00	25·00	22·72	22·73	+0·01
8.	25·00	50·00	22·72	22·74	+0·02
9.	25·00	100·00	22·72	22·72	0·00
10.	10·00	90·00	9·09	9·12	+0·03

4. *Theory of the Method.*

While the best test of a method is in its practical results, it is well to establish clearly the facts upon which it is based. Our method depends upon the following assumptions :—(1) That sulphocyanates may be decomposed at a temperature of about 100° by such concentrations of nitric acid as are insufficient either to oxidise chlorides or bromides, or to cause the volatilisation of hydrochloric or hydrobromic acid ; (2) that all but traces of the hydrocyanic acid formed by this decomposition can be volatilised during the time required for the oxidation itself ; (3) that the silver cyanide formed by addition of silver nitrate to this solution is sufficiently soluble in hot nitric acid to be separated quantitatively from the insoluble silver chloride by filtration ; and, finally, (4) that small amounts of silver cyanide do not interfere with the determination of the excess of silver by means of a sulphocyanate titration, since it acts as a soluble silver salt. Each of these assumptions has been subjected to experimental investigation.

The quantity of concentrated nitric acid used during the oxidation ordinarily amounts to 2 cc. or less. If acid should be added more rapidly than the decomposition of the sulphocyanate required, there can be present at any time not more than this small amount of acid in solutions the volume of which is usually about 200 cc. Experiments were therefore conducted to ascertain whether this amount of nitric acid could be used without loss of chlorine or bromine from solutions of the concentration used in our analytical method. 200 cc. samples of N/50 chloride solution, or N/100 bromide solution, were boiled gently for fifteen to twenty minutes with varying amounts of concentrated nitric acid, and the distillates, amounting in each case to about 15 cc., were carefully tested for the presence of the halogens. The experiments tabulated below were performed in duplicate :—

N/50 KCl. Cc.	Conc. HNO_3. Cc.	Vol. of distillate. Cc.	Cl present.
200	1·00	15	None
200	2·00	15	None
200	3·00	15	None
200	4·00	15	None
200	6·00	15	Tracer

N/100 KBr. Cc.	Conc. HNO_3. Cc.	Vol. of distillate. Cc.	Br present.
200	1·00	15	None
200	2·00	15	None
200	3·00	15	None
200	3·50	15	Traces

The results show that under the conditions of analysis, loss of halogen cannot be caused by the addition of nitric acid and boiling.

The principal, but by no means the only, decomposition product of sulphocyanic acid is hydrocyanic acid. Tests showed that when a pure sulphocyanate is decomposed in the manner described, only traces of hydrocyanic acid remain in the solution ; when the decomposition is carried out in the presence of a chloride, amounts are retained corresponding to less than 2 mgrms. of silver cyanide. This rapid loss of hydrocyanic acid during twenty minutes' treatment appeared somewhat surprising in the light of Richards and Singers' observation that the presence of chlorides prevents the expulsion of hydrocyanic acid to a marked extent (*Am. Chem. Journ.*, 1902, xxvii., 208). It occurred to us therefore that the decomposition of the sulphocyanate might possibly result in the formation of cyanogen rather than hydrocyanic acid, as was suggested by Knüpffer (*Zeit. Phys. Chem.*, 1898, xxvi., 264), who oxidised the sulphocyanate with acid potassium iodate. Accordingly, the decomposition products were passed through a solution of potassium hydroxide and the alkaline liquid analysed ; it was found to contain cyanide but no cyanate, showing the absence of cyanogen, and indicating that we had in reality to do with a very rapid expulsion of hydrocyanic acid. Richards and Singer (*loc. cit.*) expressed the view that the retention of the hydrocyanic acid by chlorides might be due to the formation of ionic complexes. Assuming this interpretation to be correct, it would appear that the complex requires a measurable time interval for its formation, and that boiling will expel hydrocyanic acid from chloride mixtures much more rapidly at the time of its formation than after the solution has been allowed to stand. It would in all probability be a lengthy operation to volatilise the acid quantitatively, but this is unnecessary in connection with our method.

The solubility of silver cyanide in nitric acid of moderate strength, which is taken advantage of in our method of analysis, was noted by Gregor (*Zeit. Anal. Chem.*, 1894, xxxiii., 33), who showed the marked solubility of the cyanide in 6 to 10 per cent acid. In hot solutions of 25 per cent strength we find its solubility much greater ; at 80° about 0·5 cc. of N 15 potassium cyanide and 0·5 cc. of N/15 silver nitrate, corresponding to about 4 mgrms. of silver cyanide, can be added to 200 cc. of the acid without causing any turbidity. The amount of hydrocyanic acid left in the solution in our method is considerably less than the equivalent of this quantity of cyanide, and there is therefore no interference with the quantitative separation of the silver chloride from the decomposition products of the sulphocyanate by filtration of a hot nitric acid solution of 25 per cent strength.

That small amounts of silver cyanide can be left in the filtrate without interference with the determination of the total silver by means of a sulphocyanate titration might be expected from the fact that in acid solution silver cyanide is much more soluble than silver sulphocyanate. Consequently, the ammonium sulphocyanate added in the titration will decompose the silver cyanide in the sense of the equation $NH_4CNS + AgCN = AgCNS + NH_4CN$, and it will not be until the ammonium cyanide reaches a considerable concentration that the reverse action will become appreciable. To ascertain how great the concentration of cyanide might safely be allowed to become, the following experiments were conducted ; a silver nitrate solution of about N/15 strength was standardised against an ammonium sulphocyanate solution, and to 15 cc. samples of the silver solution varying quantities of a N/15 potassium cyanide solution were added. In the presence of ferric iron as indicator, sulphocyanate was run into the solution until a strong red colour was obtained, the mixture was stirred briskly for five minutes to afford time for the decomposition of the silver cyanide, and then silver nitrate was run in drop by drop, with stirring, to the disappearance of colour. One drop more of the sulphocyanate gave in each case a permanent coloration. The quantity of sulphocyanate required for the total silver was then compared with the quantity as calculated from the original standardisation of the two solutions. The tabulated results show the variation in cc. from the true titre of the

solutions, the experiment being performed four times for each concentration of potassium cyanide used.

N/15 KCN taken in cc.	Extreme errors, in cc. of N/15 NH_4CNS.
0·10	−0·01 to −0·04
0·20	−0·01 to −0·06
0·30	+0·03 to −0·03
0·40	+0·05 to −0·01
0·50	+0·13 to +0·09
1·00	+0·52 to +0·12

The results show that quantities as great as 0·4 cc. of N/15 potassium cyanide solution do not affect the accuracy of the titration by amounts larger than the errors of measurement, while larger quantities cause perceptible errors in determining the true end-point. In the analytical method proposed, the amount of cyanide left in the solution is much less than half of this maximum amount.

Experiment thus substantiates the correctness of the assumptions involved in our method.

5. *Discussion of Existing Methods.*

A number of methods have been proposed for the analysis of mixtures of sulphocyanates and chlorides. The time-consuming method of Gondoin (*Zeit. Anal. Chem.*, 1897, xxxvi., 528), depending upon the precipitation and weighing of cuprous sulphocyanate, and that of Alt (*Ber.*, 1889, xxii., 3258: *Zeit. Anal. Chem.*, 1892, xxxi., 349), depending upon the oxidation of the sulphocyanate to sulphuric acid and its determination as barium sulphate, as well as the method of Krug and Ebroy (*Journ. Anal. Appl. Chem.*, vi., 184), depending upon the solubility of the salts in acetone, were not investigated.

Volhard proposed a volumetric method depending on the oxidation of the sulphocyanate by standardised potassium permanganate, assuming the correctness of the equation $NH_4CNS + 3O = NH_4CN + SO_3$ (*Ann.*, 1878, cxc., 1; *Zeit. Anal. Chem.*, 1879, xviii., 291). No analytical results accompany the publication of the method, which has nevertheless been incorporated in some text-books. An attempt to use this method resulted in complete failure. Taking a permanganate solution standardised against oxalic acid, and a sulphocyanate solution standardised against silver nitrate, effort was made to compare the two solutions by Volhard's method. The amount of sulphocyanate found varied from 86·2 per cent to 93·5 per cent of that actually present, in spite of the fact that conditions of concentration, temperature, and degree of acidity were kept as constant as possible. It was found impossible to obtain either uniformity or correctness of results. This same method has been proposed independently by Jumeau (*Bull. Soc. Chim.*, 1893, [3], ix., 346) and by Alt (*loc. cit.*), the latter stating that the method is inaccurate, but erroneously ascribing the irregularities to the iron usually present in commercial sulphocyanates.

Volhard (*Zeit. Anal. Chem.*, 1879, xviii., 291) also proposed decomposing the sulphocyanate by oxidation with dilute nitric acid at the temperature of the water-bath, then rendering the solution alkaline with ammonium hydroxide, evaporating to drive off the hydrocyanic acid quantitatively, and determining the chloride in the residual solution. Investigation of this method brought to our notice that, although the sulphocyanate is completely decomposed, as Volhard states, yet the subsequent treatment with alkali causes in part the re-formation of the sulphocyanate. This example of a reversible reaction becomes intelligible in the light of Stokes (*Journ. Am. Chem. Soc.*, 1907, xxix., 446), proof that a constant decomposition product of sulphocyanic acid is isopersulphocyanic acid, $H_2N_2C_2S_3$, which reacts with alkaline cyanides according to the equation $H_2N_2C_2S_3 + 3KCN = 3KCNS\ \ 2HCN$. In like manner other compounds containing sulphur in the lower stages of oxidation react with cyanides to form sulphocyanates; *e.g.*, Gutmann makes the reaction of thiosulphates with potassium cyanide the basis of a method for the detection of thiosulphates (*Zeit. Nahr.-Genussm*, xiii., 261; *Chem. Centr.*, 1907, i., 1152; *Chem. Abstracts*, 1907, 1447). It is clear, therefore, that any method for the analysis of the mixtures under discussion will be faulty if the solution is rendered alkaline before complete oxidation of the sulphur, which operation was found by Treadwell to require two hours when the oxidising agent was fuming nitric acid ("Analytical Chem.," ii., p. 261, New York, 1906).

Borchers (*Zeit. Anal. Chem.*, 1883, xxii., 92; *Borchers' Repert. Anal. Chem.*, 1881, 130; Treadwell's "Anal. Chem.," ii., p. 261) proposes the precipitation of chloride and sulphocyanate as their silver salts, and the determination of their sum by Volhard's method; the precipitate is then washed into a flask with a stream of concentrated nitric acid, and boiled with that reagent for three-quarters of an hour to the complete decomposition of the silver sulphocyanate; the solution is diluted and filtered, and the silver determined in the filtrate. Experience showed that the long boiling with concentrated nitric acid renders the method entirely unsuited for ordinary laboratory use.

Barnes and Liddell (*Journ. Soc. Chem. Ind.*, 1883, ii., 122) precipitate the sulphocyanate as its cuprous salt by titration with copper sulphate in the presence of a bisulphite, the end-point of the reaction being determined by a drop test with potassium ferrocyanide. The authors note that the end-point cannot be determined exactly owing, as they state, to the oxidation of the copper in the cuprous sulphocyanate and its reaction with the ferrocyanide. We were unable to devise any method for rendering the determination of the end-point more exact, and found the method of use only for approximating the correct values.

Diehl (*Chem. Centr.*, 1883, 649; *Ber.*, 1883, xvi., 2319) also precipitates the sulphocyanate as its cuprous salt, using excess of copper sulphate and a bisulphite, filters off the precipitate, and determines the chloride in the filtrate. Noyes and Abbot (*Zeit. Phys. Chem.*, 1895, xvi., 129) investigated this method, and found variations between +0·27 per cent and −0·49 per cent in the amount of chlorides found; the method can therefore not be regarded as exact. Mann (*Zeit. Anal. Chem.*, 1889, xxviii., 668) has proposed a substitution of hydrogen sulphide for the bisulphite as a reducing agent; his results for the chloride vary from the true figures by −0·3 per cent to −2·8 per cent.

Incidentally to a physico-chemical research Knüpffer (*Zeit. Phys. Chem.*, 1898, xxvi., 262) proposed the oxidation of the sulphocyanate by acid potassium iodate. After boiling off the hydrocyanic acid, or cyanogen, as he believes it to be, he reduces the excess iodate with sulphur dioxide, oxidises with a nitrite, and boils again to expel the iodine completely; the chloride is determined in the residue. The figures given indicate that the method is accurate; it is made very tedious, however, by the repeated boilings necessary for quantitative expulsion of the hydrocyanic acid and the iodine.

The method of Rupp and Schied (*Ber.*, 1902, xxxv., 2191), depending upon the oxidation of the sulphocyanate by free iodine in bicarbonate solution and titration of the unused iodine, was shown by Thiele (*Ber.*, 1902, xxxv., 2766) to be inaccurate, owing to the incomplete oxidation of the sulphocyanate in the half-hour's time proposed by Rupp and Schied. Thiele states that if the oxidation be continued for four hours the results are accurate; in this modified form Rupp has adopted the method, and claims good results from its use (*Arch. Pharm.*, 1905, ccxliii., 468; *Journ. Am. Chem. Soc.*, 1906, xxviii., 1771; *Journ. Chem. Soc.* (Abstracts), 1905, lxxxviii., 867). In view, however, of Stokes' results on the decomposition of sulphocyanates and Treadwell's statement that complete oxidation to sulphuric acid requires the most vigorous treatment with fuming nitric acid, it may be doubted whether the oxidation by iodine follows quantitatively the simple equation expressed.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 21st, 1907.

Sir WILLIAM RAMSAY, K.C.B., F.R.S., President, in the Chair.

(Concluded from p. 291).

236. "*Mercurous Hyponitrite.*" By EDWARD DIVERS.

A paper with the above title, by P. C. Rây, published in the August number of the *Transactions*, having been taken as read, opens with the following words: "Mercurous hyponitrite, which has already been obtained in a somewhat impure condition by the author (*Trans.*, 1897, lxxi., 348), may be prepared (*a*) by precipitating mercurous nitrate with carefully neutralised sodium hyponitrite made according to Divers' method (*Trans.*, 1889. lxxv., 96, 119); (*b*) by precipitating mercuroso-mercuric nitrite (Rây, *Trans.*, 1902, lxxxi., 644) with the crude alkaline hyponitrite; or (*c*) by precipitating mercurous nitrate with acid potassium hyponitrite (Thum, *Inaug. Dissert.*, 1893)." Any one unacquainted with the facts referred to will hardly get a correct notion of them from this obscure sentence. These facts are (1) that Thum, in an unusually brilliant inaugural dissertation on hyponitrous acid, gave, in 1893, a description, accompanied by excellent analyses, of the mercurous salt among others; (2) that, in 1897, there appeared a paper by Rây describing, as new, mercurous hyponitrite (in admixture with a mercuric salt) obtained from sodium hyponitrite by adding it to a solution of mercuroso-mercuric nitrite, a solution he had resort to (notwithstanding the complications likely to ensue consequent upon the presence in it of mercuric salt and upon its being a solution of a nitrite) because he supposed that mercurous nitrate would not serve for the purpose, in consequence of the acidity of its solution; and (3) that, beyond this pointless substitution of a solution of one mercurous salt for another, Rây's paper contained nothing new, nothing so good as had been already published, and yet something beneath criticism about a supposed mercuric hyponitrite (see *Trans.*, 1899, lxxv., 119).

Rây's recent paper, besides implying that mercurous hyponitrite, prepared by Rây's reagent, has now been obtained free from mercuric salt in some way not even alluded to (the evidence for this being some new analyses, three out of four of which are not a whit better than those of the admittedly impure preparations), contains only the statement that this preparation of Rây's (possibly containing nitrite) cannot be dissolved in nitric acid without immediately yielding metallic mercury, notwithstanding the fact that Thum was able to reprecipitate the salt in a pure state from its solution in nitric acid, as his analysis and description establish, and that the writer (*Trans.*, 1899, lxxv., 121) has published experience similar to Thum's, each working with salt of high purity.

237. "*Decomposition of Mercurous and Silver Hyponitrites by Heat.*" By EDWARD DIVERS.

Rây and Gañguli have not succeeded in giving a definite and consistent interpretation of the results which they have recorded in their recent paper on the decomposition of mercurous and silver hyponitrites by heat (*Trans.*, 1907, xci., 1397). They have not perceived that these results are impossible as they stand, and must be corrected if they can be. The corrections called for in the case of the silver salt lie well within the limits of errors in the experimental analyses, whilst, in the case of the mercury salt, the justifiable assumption of the presence of nitrite fairly well accounts for numbers otherwise too far from what the pure salt would have given. Had the authors been aware of the imperfect nature of their results, in the case of the mercury salt, they would presumably have deferred publication of them. But, even as published, these results seem capable of such revision and subsequent interpretation as may make them add materially to the knowledge of the decomposition of hyponitrites by heat.

The two hyponitrites examined evidently decompose when heated each in three ways, which are expressed by the following equations. For the mercury salt, these are: $(HgON)_2 = 2Hg + 2NO$ (1); $(HgON)_2 = Hg + HgO + N_2O$ (2); $3(HgON)_2 = 4Hg + (HgNO_3)_2 + 2N_2$ (3). In Rây and Gañguli's mode of procedure, it would seem, on probable calculation, as tabulated below, that 2·96 out of 6·09 parts of the salt will have decomposed according to (1), 2·32 parts according to (2), and 0·81 part according to (3). Or, in percentage numbers, 48·6, 38, and 13·3 according to Equations (1), (2), and (3) respectively.

In the case of the silver salt, where we are on much surer ground, two of the equations are just like (1) and (3) for the mercury salt, whilst the other, which only differs from (2) as given for the mercury salt because of the instability of silver oxide, is $(AgON)_2 = 2Ag + O + N_2O$ (2'), the free oxygen of which with 2NO by Equation (1) becomes first N_2O_3, let us say, and then nitrite, on contact with the solution of potassium hydroxide, as Rây and Gañguli explain. Ultimately, therefore, the second equation becomes $2(AgON)_2 = 4Ag + N_2O_3 + N_2O$, but, for the sake of comparison with the mercury salt, it seems better to use the equation showing free oxygen and count the nitrite nitrogen along with that as nitric oxide. The conclusion that must be come to, after inspecting the tables, will be that Rây and Gañguli had really 7·84 (6·58 + 1·26) parts out of 10·15 of the silver salt decomposed according to equation (1); 1·26 parts according to (2'), and 1·05 parts according to (3) (Ag being read for Hg). Or, 83, 13·3, and 3·7 per cent respectively according to Equations (1), (2'), and (3). Reference to the authors' paper will show that they have themselves put forward Equations (1) and (2), that they reject (3), and that they suggest others which, it may here be said, could not be worked in with their results in any likely way.

The interpretation, here submitted, of the effects of heating the two hyponitrites is derived from the numbers exhibited in the subjoined tables.

Distribution of the Nitrogen and Oxygen of Mercurous Hyponitrite in the Products of its Decomposition by Heat.

Product.	Found. N.	Found. O.	Calculated. N.	Calculated. O.
N_2	0·54	—	0·54	—
N_2O . ..	2·32	1·33	2·32	1·33
NO	2·53	2·89	2·96	3·38
N_2O_3 ..	0·24	0·41	—	—
NO_3 . ..	0·48	1·65	0·27	0·92
HgO ..	—	1·19 (*a*)	—	1·33
Total ..	6·11	7·47	6·09	6·96
Theory.	6·09	6·96	6·09	6·96

Distribution of the Nitrogen and Oxygen of Silver Hyponitrite in the Products of its Decomposition by Heat.

N_2	1·06	—	0·70	—
N_2O . ..	1·15	0·66	1·26	0·72
NO	6·58	7·52	6·58	7·52
N_2O_3 ..	1·26	2·16	1·26	2·16
NO_2 ..	0·35	1·20	0·35	1·20
Total ..	10·40	11·54	10·15	11·60
Theory.	10·15	11·60	10·15	11·60

(*a*) See note on p. 1400 in Rây and Gañguli's paper.

The numbers in the first column of each table are the mean numbers of those given by the authors for the nitrogen of the several products as parts per cent of the salt. The fourth line ("N_2O_3") shows the nitrogen of the nitrite in the potassium hydroxide solution they made use of. The fifth line ("NO_3") shows the nitrogen, obtained or calculated, as mercurous or silver nitrate. In the case of the mercurous hyponitrite, the distribution of the nitrogen

as nitrite and nitrate has been assumed to have been in all three experiments as 1 : 2, in agreement with what it was found to be in the only reported experiment in which it was determined by the authors.

The numbers in the second column of each table are for the oxygen corresponding with those for the nitrogen in the first column. Their sum, in the case of the mercury salt, is much in excess of the percentage of oxygen in mercurous hyponitrite. Since the mercurous hyponitrite, which the authors made use of, had been prepared from mercuroso-mercuric nitrite, the excess of oxygen found may be attributed to the presence of nitrite in the salt as prepared. The sixth line ("HgO") shows the oxygen left as mercuric oxide as being necessarily equal to that in the nitrous oxide, less (in the second column) by one-third of that as nitrous anhydride ($1{\cdot}33 - 0{\cdot}14 = 1{\cdot}19$).

The numbers in the third and fourth columns of each table have been calculated in accordance with the equations already given, and in such a way as to make them differ the least possible from the numbers furnished by the experiments, under the necessary condition that their respective sums shall be identical with the percentages of nitrogen and oxygen in the pure mercurous and silver hyponitrites. In the case of the mercury salt, it has been assumed that, when free from nitrite, mercurous hyponitrite yields no red fumes and very little nitrate, which is in accordance with the writer's experience, referred to by the authors. The numbers for the silver salt have been altered to make the free nitrogen equal to only twice that found as nitrate; that found as nitrous oxide to be equal to that as nitrite, and total nitrogen and oxygen to be equal respectively to the percentages of these elements in the pure salt.

A noticeable point in Rây and Gañguli's paper is their experience of the conversion by heat of nearly one-eighth of silver hyponitrite into silver, nitrous oxide, and oxygen. The writer did not observe the presence of any nitrous oxide in his experiments (*Trans.*, 1899, lxxv., 108). Nor has any other worker recorded the fact of having done so. On the evidence afforded by Rây and Gañguli's experiments, the writer is prepared to admit that nitrous oxide may never be absent altogether in the products of the decomposition of silver hyponitrite by heat. As to the matter of quantity of nitrous oxide, the details of their experiments and his are sufficiently different to account for the fact of their obtaining so much of it and he so little as to pass unnoticed. The salt they used contained, they think, impurities enough to be mentioned, and began to decompose very slowly at 100°, and at 140° suffered rapid decomposition. It had been dried cold over sulphuric acid under reduced pressure, but was heated to decomposition in a tube between which and the Sprengel pump a tube of "aqueous potash" intervened. A very little moisture would have given a lower temperature of decomposition, and caused free generation of nitrous oxide. In the writer's experiments, salt of high purity, dried finally in a Sprengel vacuum at 98°, was used. Thus dried, the pure salt hardly begins to decompose at 140°, and is not in free decomposition much, if at all, below 160°. It would seem highly probable from the difference in the effects of heat that the generation of nitrous oxide is largely, if not wholly, a matter of hydrolysis.

Another point worthy of attention in Rây and Gañguli's paper is their contention that nitric peroxide is a secondary product arising out of the union of nitric oxide with the oxygen set free along with nitrous oxide. The writer thinks this to be highly probable. His position as to nitric oxide and nitric peroxide being primary products has been that for twenty years he held, without proof, that nitric oxide was the primary product which produced red fumes by contact with air. Thum proved, in 1893, that out of contact with air the salt still gave nitric peroxide when heated. The writer then examined the matter himself for the first time and found Thum right. Having ascertained that nitric peroxide and silver gave silver nitrate and nitric oxide, he concluded, in 1899, that nitric peroxide was the primary product and nitric oxide secondary. Now he returns to his first view and agrees with Rây and Gañguli that nitric oxide is the primary product, at the same time being certain that it is also reproduced by reduction of the nitric peroxide by silver.

It is much to be desired that Rây and Gañguli would repeat their experiments, making use of pure mercurous hyponitrite prepared by Thum and the writer's process, and of the driest pure silver hyponitrite, in their apparatus supplied with some solid potassium hydroxide in the near end of their absorption tube.

238. "*Cupric Nitrite.*" By EDWARD DIVERS.

A paper appeared not long ago in the *Transactions* (1907, xci., 1405) on cupric nitrite, in which Rây sets forth his observations on what he regards as being the atmospheric oxidation and autoxidation of this salt. Now nitrites, as such, do not oxidise, and, in the cases where they do not hydrolyse in water, they are stable in solution. (The passage of cobaltous into cobaltic nitrite is, of course, no exception to the statement.) What Rây has occupied himself with is simply the oxidation of nitrous acid, not cupric nitrite, in aqueous solution. For when a cupric salt is dissolved in water, it is always hydrolysed to some extent, as is shown by its acid reaction and other facts. Nitrous acid in aqueous solution becomes nitric acid and nitric oxide, and nitric oxide oxidises in the air. When it is added that nitric acid decomposes some of the cupric nitrite to form nitrate together with more free nitrous acid, there seems to be no more to be said. As to the oxidation of cupric nitrite, as such, we are left as we were, without any evidence whatever of its occurrence.

NOTICES OF BOOKS.

Steel Works Analysis. By JOHN OLIVER ARNOLD and F. IBBOTSON. Third Edition. London and New York: Whittaker and Co. 1907.

THIS book is intended specially for the use of assistants in steel works, and for students who wish to fit themselves for posts in steel works' laboratories, or who, having a fair knowledge of pure chemistry, wish to specialise in the analytical investigation of irons and steels. Only those processes are discussed which give accurate results, and a great choice of methods is avoided in favour of the plan of giving only one or two really reliable methods of determining each important constituent. The description of each process is clearly arranged in such a way that the student is practically forced to keep the theoretical reason for every step well in mind, and preserved from merely adding certain reagents or subjecting his sample to specified operations mechanically. The approximate time taken for each experiment is stated. In the third edition gas analysis is treated more fully than before, and the section on the calorimetry of fuels has also been enlarged and brought up to date. In addition the analysis of brasses, bronzes, and white metals is now included, and every part of the book has been carefully revised.

Electric Power and Traction. By F. H. DAVIES, A.M.I.E.E. London: Archibald Constable and Co., Ltd. 1908.

A KNOWLEDGE of the possibilities of electric traction and the application of electric power in general has become almost indispensable to many classes of students, members of allied trades, and engineers, and this book will fulfil a useful purpose if it enables such readers to get a practical insight into the generation and distribution of power and its application under various circumstances. The author appears to have chosen his subjects exceedingly well, and has contrived to make his book interesting, while at the same time he has not entirely avoided technical details. The various systems adopted in electric traction are fully

discussed and illustrated, and the advantages and disadvantages of three-phase and one-phase motors are weighed. A useful glossary of the terms which might possibly be unfamiliar to the student who has not had any special training in electrical engineering adds greatly to the usefulness of the book.

A History of Hindu Chemistry. By Praphulla Chandra Ray, D.Sc. Second Edition. London: Williams and Norgate. 1907.

The second edition of this work, which had a very favourable reception at the hands of orientalists and others, contains some important additional matter which shows clearly that the sciences of chemistry and medicine were developed earlier among the Hindus than among the Greeks. The book contains copious quotations from Sanskrit texts, and the author has collected valuable information from rare manuscripts relating to the origin of Hindu chemistry. The book is one which hardly appeals to the general student of chemical history, but at the same time the author's acquaintance with scientific knowledge among the Hindus is probably unique, and his book will command the attention of all who are making a special study of the early history of the science.

La Bibliographie Industrielle. ("The Industrial Bibliography.") By Jules Garçon. Paris: 40 bis, Rue Fabert. 1907.

This essay on the practical value of a scientific and industrial bibliography gives many examples of the hindrances which the lack of a comprehensive and classified index puts in the way of scientific work, and shows clearly what great benefits such an index would confer on inventors and others. There is no need for the author to emphasise the many difficulties which those who want to look up some special question encounter when they are forced to consult the scattered literature in different languages which may contain references to the work they have in hand, and it is universally recognised that a trustworthy index would be a great convenience. In the essay suggestions are made as to the most satisfactory basis of a complete bibliography, and details of the best arrangement and division of subjects are included, with some hints about the preparation of summaries of the papers catalogued.

CORRESPONDENCE.

ALUMINIUM CARBIDE.

To the Editor of the Chemical News.

Sir,—My attention has been drawn to a letter on the subject of aluminium carbide, by Messrs. Ellis and Weston, which appeared in the Chemical News of November 29th (vol. xcvi., p. 270).

Having carried out in the Electro-chemical Laboratory of Dr. Hutton, Manchester University, in the autumn of 1904 and subsequently, an extended investigation of the formation of this compound, I should like to point out that, although the formation of aluminium carbide was carried out in a variety of ways and at different temperatures, no evidence was obtained of the existence of any other carbide than that represented by the formula Al_4C_3. The only gases evolved from the product on treatment with dilute HCl were methane and hydrogen, the latter from the unchanged aluminium, with only a trace of other gases due to impurities in the aluminium, such as always give an odour to hydrogen evolved when acids act on metals. My experiments were chiefly carried out to find the *rôle* played by carbon monoxide in the formation of carbide.—I am, &c.,

W. H. Patterson.

Heriot-Watt College, Edinburgh.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlv., No. 21, November 18, 1907.

Presence of Paramethoxycinnamic Aldehyde in Essence of Tarragon, and some Derivatives of Tarragol.—Maurice Daufresne.—Essence of tarragon, on repeated fractionation under reduced pressure, gives a yellow oil, which in all its reactions resembles paramethoxycinnamic aldehyde, $O.CH_3—C_6H_4—CH = CH—CHO$. The same aldehyde can be prepared by condensing anisic aldehyde and acetaldehyde in presence of caustic soda. The fixation of one molecule of hypoiodous acid by tarragol in presence of ether which has been freed from alcohol and saturated with water, leads to the formation of the monoiodohydrine of *p*-methoxyphenylpropane diol, $O.CH_3—C_6H_4—CH_2—CH.OH—CH_2I$. When tarragol is subjected to the action of iodine and mercuric oxide in absolute methyl alcohol the methyl iodohydrine is formed, $O.CH_3—C_6H_4—CH_2—CH(O.CH_3)—CH_2I$.

No. 22, November 25, 1907.

Nitrous Isomerisation of Isobutyl Alcohol.—Louis Henry.—By the action of metallic nitrites upon the chlorhydrate isobutylamine is converted into a mixture of which three quarters is tertiary butyl alcohol and one quarter isobutyl alcohol. The methylated homologues of the salts of ethylamine under the same conditions invariably give alcohols which do not correspond exclusively to the amine used, and the quantity of alcohol produced by this isomerisation increases in proportion as the methylic substitution is more complete; *i.e.*, as the hydrogen is scarcer in the system adjacent to the complex $H_2C—(NH_2)$, at the expense of which the alcohol, the final product of the reaction, is formed. This nitrous isomerisation of alcohols is analogous in many ways to the isomerisation of haloid ethers under the action of heat.

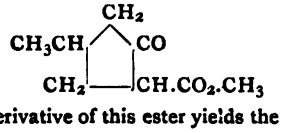
Uranium Tetraiodide.—Marcel Guichard.—The author has prepared the anhydrous tetraiodide of uranium in sealed exhausted tubes by heating iodine to 180° and letting the vapour act upon uranium heated to 500°. The iodide is a crystalline mass, fusing at about 500°. Its specific gravity is 5·6 at 15°. When heated in hydrogen it gives up iodine. Chlorine decomposes it in the cold. When it is heated gently in dry oxygen it takes fire, and is converted into the green oxide, U_3O_8. The same reaction occurs when it is heated in dry air. It also loses iodine, and absorbs oxygen when kept at the ordinary temperature in dry air. In damp air it deliquesces and forms a brown liquid, which contains free iodine, and if after some hours excess of water is added a yellow solution is obtained which when heated gives a precipitate of green hydrated oxide. The tetraiodide dissolves easily in water, and in absence of oxidising agents gives a green acid solution. The analysis of the iodide agrees closely with the formula UI_4.

Synthesis of Ammonia from its Elements by Catalysis.—Léon Brunel and Paul Woog.—The authors prepared mixtures of nitrogen and hydrogen (1 vol. to 3 vols.), and passed them at different temperatures and with different velocities over substances which would be likely to act as catalysers. With finely-divided carbon, obtained by the decomposition of toluene or carbon dioxide by reduced nickel, no ammonia is formed between the temperatures of 170° and 285°. But if under the same conditions the nitrogen in the gaseous mixture is replaced by air a certain amount of carbon burns, and the heat disengaged by this reaction leads to the formation of small quantities of ammonia.

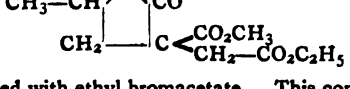
Method of Determining very Small Quantities of Zinc.—Gabriel Bertrand and Maurice Javillier.—A complex mixture of Sn, Sb, As, Cu, Cd, Co, Pb, Ag, Fe, Mn, Zn, Al, Ba, Ca, Mg, Na, K as carbonates, chlorates, sulphates, nitrates, phosphates, silicates, and sulphides, is treated with aqua regia, evaporated, taken up with dilute hydrochloric acid, and precipitated with sulphuretted hydrogen. The filtrate is boiled, ammonia is added and hydrogen peroxide. The precipitate which forms is again dissolved in hydrochloric acid, and re-precipitated with ammonia and H_2O_2. The liquids then contain all the zinc. They are boiled, and enough milk of lime is added to liberate all the ammonia and precipitate all the zinc as zincate. The calcium zincate is treated with hydrochloric acid, thus giving zinc chloride and calcium chloride, and the zinc is precipitated with sulphuretted hydrogen. This method is sufficiently sensitive to enable 0·1 mgrm. of zinc to be determined in 3 litres of solution. Nickel and cobalt follow zinc in these reactions, and the method is therefore not applicable when they are present.

Two Isomeric Methyl Sparteïns.—Charles Moureu and Amand Valeur.—Two definite chemical products can be isolated by decomposing the hydrate of α-methyl sparteïnium. When the mixture of the products is treated with methyl iodide 30 per cent does not undergo methylation. This part is α-methyl sparteïn. β-Methyl sparteïn is transformed into iodo-methylate from which it is difficult to isolate the base. The fractional crystallisation of the di-iodohydrates prepared from the raw base enables the separation of the less soluble α-methyl sparteïn di-iodohydrate to be effected quite easily. If the raw base is heated on a water-bath with a slight excess of normal sulphuric acid, only the sulphate of α-methyl sparteïn isomerises to sulphomethylate, and the action of alkali liberates the bases which have not isomerised. By fractionating the mono-iodohydrates of these last bases a definite mono-hydrate can be isolated, and from it β-methyl sparteïn can be extracted. α- and β-Methyl sparteïns are unsaturated bases which energetically reduce potassium permanganate in acid solution at 0°. In both of them the methyl group is bound to the nitrogen. They differ essentially from one another in the fact that α-methyl sparteïn alone isomerises under certain conditions to saturated derivatives.

Synthesis of β-Campholene Lactone from the Lactone of 2—4-Dimethyl 2-Cyclopentanol 1-Acetic Acid.—G. Blanc.—Methyl β-methyl adipate condenses under the action of sodium, giving methyl cyclopentanone carbonic esters of formula—



The sodium derivative of this ester yields the condensation product—



when treated with ethyl bromacetate. This compound is hydrolysed by boiling hydrochloric acid to 4-methyl 2-cyclopentanone 1-acetic acid, the methyl ether of which yields β-campholene lactone.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xl., No. 14, 1907.

Hydroxy - aquo - tetrammino - colbatic Salts.—A. Werner.—Diaquo-tetrammino-cobaltic chloride when dissolved in concentrated ammonia and precipitated with alcohol readily gives the hydroxy salt, $\left[\begin{matrix}HO\\H_2O\end{matrix}Co(NH_3)_4\right]Cl_2$, from which other salts of the same series can be prepared. They are bluish or reddish purple in colour, and have an alkaline reaction in aqueous solution. With ammonium salts they give diaquo-tetrammino-cobaltic salts,—

$$\left[\begin{matrix}HO\\H_2O\end{matrix}Co(NH_3)_4\right]X_2+NH_4X=$$
$$=\left[\begin{matrix}H_2O\\H_2O\end{matrix}Co(NH_3)_4\right]X_3+NH_3.$$

They are unstable in aqueous solution, their colour changing in a short time to red-brown, which finally darkens, and black or brown crystals of the dodecammino-hexol-tetra-cobaltic series, $\left[Co\left[\begin{matrix}HO\\HO\end{matrix}Co(NH_3)_4\right]_3\right]X_6$, separate.

Hydroxy - nitro - tetrammino - cobaltic Salts.—A. Werner.—The aquo-nitro-tetrammino-cobaltic salts give with ammonia the following reaction:—

$$\left[\begin{matrix}H_2O\\O_2N\end{matrix}Co(NH_3)_4\right]X_2NH_3=$$
$$=\left[\begin{matrix}HO\\O_2N\end{matrix}Co(NH_3)_4\right]X+NH_4X.$$

The chloride, nitrate, and bromide of this latter series all crystallise with 1 molecule of water. Their aqueous solutions are alkaline, and they absorb carbon dioxide from the air when moist, the following reaction occurring in the case of the nitrate:—

$$\left[\begin{matrix}HO\\O_2N\end{matrix}Co(NH_3)_4\right]NO_3+CO_2=$$
$$=\left[\begin{matrix}HO_2CO\\O_2N\end{matrix}Co(NH_3)_4\right]NO_3.$$

This reaction shows that the constitution of the salt is correctly represented by the formula. If it were an aquo - salt the reaction would be $\left[\begin{matrix}H_2O\\O_2N\end{matrix}Co(NH_3)_4\right]\begin{matrix}OH\\NO_3\end{matrix}+CO_2=\left[\begin{matrix}H_2O\\O_2N\end{matrix}Co(NH_3)_4\right]\begin{matrix}CO_3H\\NO_3\end{matrix}$, and the carbon dioxide ion could be detected in the resulting product, which is not the case.

Anomalous Inorganic Oxonium Salts; a New Class of Basic Salts.—A. Werner.—The author has already described two classes of basic salts, namely, those in which the hydroxyl groups are bound non-ionogenically with the metallic atoms, *e.g.*, $\left[Co\begin{matrix}OH\\(NH_3)_5\end{matrix}\right]X_2$, and, secondly, the *ol*-salts, in which the hydroxyl group forms a link between two metallic atoms, *e.g.*, $\left[Co\left[\begin{matrix}OH\\OH\end{matrix}Co(NH_3)_4\right]_3\right]X_6$. When either ammonium chloride, iodide, or bromide acts on the hydroxy-nitro-tetrammino-cobaltic salts a third series of salts, *e.g.*, $\left[Cl(H_3N)_4Co\begin{matrix}OH\\NO_2\end{matrix}\right]_2HCl+4H_2O$, is obtained. These salts resemble the anomalous organic oxonium salts, and their existence is an important argument against the assumption of tetravalent oxygen in oxonium salts.

Chloro - nitro - tetrammino - cobaltic Salts.—A. Werner.—Chloro - nitro - tetrammino - cobaltic chloride is very rapidly hydrated when dissolved in water, and even if nitric or sulphuric acid is immediately added only aquo salt can be separated. If, however, the chloride is poured on to a filter with ice-cold water, and the filtrate is allowed to drop into the cooled reagent, the hydration process can be arrested, and chloro-nitro-tetrammino salts separate. Thus it has been found that the chloride precipitated by potassium chloride from a solution of aquo-nitro-tetrammino salts is an esohydrate of chloro-nitro-tetrammino-chloride, *i.e.*, $\left[\begin{matrix}Cl\\O_2N\end{matrix}Co(NH_3)_4\right]Cl+H_2O$. (An esohydrate is one in which the water molecule does not form part of the inner nucleus of the complex radicle). Aquo compounds are the more unstable the more strongly basic is

the hydroxy compound in aqueous solution, as the following scheme shows :—

$$\left[\begin{matrix}O_2N\\Cl\end{matrix}Co(NH_3)_4\right]Cl_2 + H_2O \rightleftarrows \left[\begin{matrix}O_2N\\H_2O\end{matrix}Co(NH_3)_4\right]Cl_2;$$

Very quickly.

$$\left[\begin{matrix}O_2N\\HO\end{matrix}Co(NH_3)_4\right]Cl.$$ Strong base; precipitates AgO.

$$\left[\begin{matrix}Cl\\H_2O\end{matrix}Co(NH_3)_4\right]Cl_2 + H_2O \rightleftarrows \left[\begin{matrix}H_2O\\H_2O\end{matrix}Co(NO_3)_4\right]Cl_3;$$

Much more slowly.

$$\left[\begin{matrix}H\\H_2O\end{matrix}Co(NH_3)_4\right]Cl_2.$$ Weaker base; sets NH_3 free from ammonium salts.

$$\left[\begin{matrix}Cl\\ON\end{matrix}Ru(NH_3)_4\right]Cl_2 + H_2O \rightleftarrows \left[\begin{matrix}H_2O\\ON\end{matrix}Ru(NH_3)_4\right]Cl_3;$$

Exceedingly slowly.

$$\left[\begin{matrix}HO\\ON\end{matrix}Ru(NH_3)_4\right]Cl_2.$$ Neutral.

$$\left[\begin{matrix}Cl\\Cl\end{matrix}Pt(NH_3)_4\right]Cl_2 + H_2O \rightleftarrows \left[\begin{matrix}H_2O\\H_2O\end{matrix}Pt(NH_3)_4\right]Cl_4;$$

Does not take place.

$$\left[\begin{matrix}HO\\HO\end{matrix}Pt(NH_3)_4\right]Cl_2.$$ Neutral.

This explains why salts such as potassium chloride and sodium chloride undergo a momentary electrolytic dissociation when they dissolve in water, although they always separate from solutions in the anhydrous form. In these chlorides, which are derived from the strongly basic alkaline hydroxides, the processes of hydration and dehydration take place so quickly that they cannot be detected by any known method.

Theory of Bases.—A. Werner.—One of the most important results of the author's investigation of the hydroxy metallic ammonia compounds is the discovery that these compounds are simply special cases of the group of metallic hydroxides, and behave like salts; *i.e.*, the hydroxyl groups bound directly to the metal cannot be ionised, and the electrolytically dissociated part of the hydroxy compounds is present in aqueous solution as hydroxide of the aquo-compound :—

$$\left[Co\begin{matrix}OH\\(NH_3)_5\end{matrix}\right]Cl_2 + H_2O \rightarrow \left[Co\begin{matrix}OH_2\\(NH_3)_5\end{matrix}\right]OH\,Cl_2.$$

Hydroxy-compound (OH non-dissociating). Aquo-compound (OH dissociating).

The hydroxy compound may be called an anhydro-base and the aquo compound an aquo-base. Then any compound which combines with water to give a hydrate, which dissociates in aqueous solution into a complex positive ion and hydroxyl ions, is an anhydro-base, while all water addition products giving hydroxyl ions in aqueous solution are aquo or true bases. The stability of the aquo salts varies with the nature of the acid radicle and of the base, and generally the aquo salt is more unstable the stronger the acid is.

Behaviour of Sulphur towards Water, and the Vapour Pressure of Sulphur from 78° to 210°.—Otto Ruff and Hugh Graf.—To investigate the behaviour of sulphur towards water vapour the authors have compared the partial pressure of sulphur in an indifferent gas and in water vapour. If a reaction with water occurs according to the equation $2H_2O + S_3 = 2H_2S + SO_2$, as Cross and Higgin state, the partial pressure in water vapour would be greater than in an indifferent atmosphere. Carbon dioxide was used to test this statement, and the vapour pressures were measured between 78° and 210° by the dynamical method. It was found that the partial pressures in water vapour and in carbon dioxide were the same, and that consequently there can be no appreciable reaction between sulphur and water. The following table shows the vapour pressures at different temperatures :—

Temperature.	Vapour pressure.
78°	0·002 mm.
104°	0·01 ,,
135°	0·1 ,,
181°	1·0 ,,
245°	10 ,,

MEETINGS FOR THE WEEK.

Saturday, 28th.—Royal Institution, 3. (Christmas Lectures, adapted to a Juvenile Auditory). "Astronomy, Old and New," by Sir David Gill, K.C.B., F.R.S., &c.

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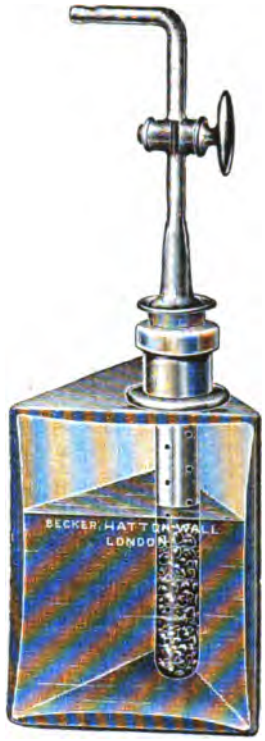

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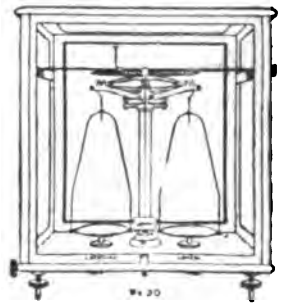

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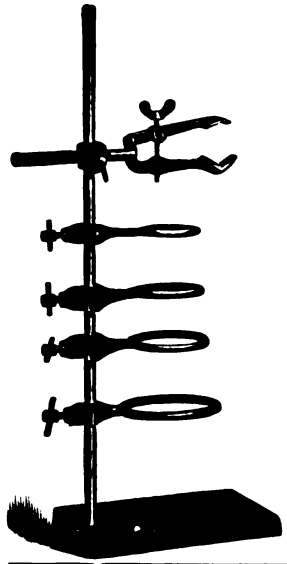

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THE CHEMICAL NEWS.

Vol. XCVI., No. 2509.

THE ESTIMATION OF CELLULOSE IN WOOD BY THE CHLORINATION METHOD.

By A. L. DEAN and G. E. TOWER.

The chemical constitution of woody tissues presents a problem of great complexity. Any single sample of wood contains a number of complex compounds whose nature is but little understood. If all kinds of wood were chemically alike, or even if the wood from all parts of the same tree was identical, the study of woody tissue would be simplified. The older idea, especially the idea prevalent amongst botanists, was that the cell walls of woody tissues were composed of "cellulose" which became impregnated with "lignin." Later and more careful studies appear to have established the fact that the foundation of woody cell walls is not a simple cellulose, but a compound cellulose, to which the name lignocellulose has been given. This lignocellulose may be split up into cellulose on the one hand and the lignone group on the other. The cellulose which results from the cleavage differs to a marked extent from the normal type cellulose of the cotton fibre. The lignone complex appears to contain cyclical groups and to be related to the carbohydrates in no very definite fashion.

Besides the lignocellulose which makes up the major portion of wood, there are always present a number of different bodies which are apparently not chemically united to the lignocellulose. Amongst these substances two are prominent; the so-called wood gum, which may be extracted with cold dilute alkaline solutions, and the group of the ether soluble resins.

It was stated above that the lignocellulose might be split into the two constituent radicals, cellulose and lignone. This cleavage is not easily carried out quantitatively, inasmuch as the treatments which remove the lignone tend to attack the cellulose. The isolation of cellulose from wood is carried out on an enormous scale in the manufacture of paper-pulp by the sulphite and soda processes. These methods are said to always involve some loss of cellulose, and unless carefully regulated the loss is likely to be great.

A number of methods have been elaborated for the estimation of the quantities of cellulose in vegetable cell walls. They are all tedious, and the cellulose obtained by several of them is apparently a variable and ill-defined product. Cross and Bevan have elaborated a method for the estimation of cellulose in the lignocellulose of jute fibre, a method which appears to yield concordant and valuable results ("Cellulose—an Outline of the Chemistry of the Structural Elements of Plants," Cross and Bevan, London, 1895). In their method the lignocellulose is treated with chlorine gas, giving rise to a lignone chloride which is soluble in hot alkaline sulphite solutions. They do not give the results of the systematic application of this method to cellulose estimations in wood, although they imply that it is applicable to such tissues.

Sherman (*Journ. American Chem. Soc.*, 1897, xix., 291), in his study of the insoluble carbohydrates of the wheat, estimated the amount of cellulose in the lignocellulose of the wheat kernel. After trying out the methods of Schulze (potassium chlorate and nitric acid), Lange (fusion with caustic alkalis), and the chlorination method of Cross and Bevan, Sherman concludes that this last method gives the most exact estimate of the cellulose and yields cellulose of maximum purity.

Cross and Bevan give the following directions ("Cellulose," p. 95):—"About 5 grms. of the fibre weighed after drying at 100° are—(*a*) boiled for thirty minutes with a dilute solution of sodium hydrate (1 per cent NaOH), which is kept at constant volume by addition of water. The fibre is well washed on a cloth or wire gauze filter, squeezed to remove excess of water, opened out, placed in a beaker, into which (*b*) a slow stream of washed chlorine gas is passed. Rapid reaction ensues, and the fibre changes in colour from brown to a bright golden yellow. To ensure complete conversion of the lignone, it is necessary to leave the fibre for some time (from thirty to sixty minutes) in the atmosphere of Cl gas. (*c*) The chlorinated fibre is removed, washed once or twice with water to remove hydrochloric acid, and placed in a 2 per cent solution of sodium sulphite; the solution is gradually raised to the boiling point, a small quantity of caustic soda solution is added (0·2 per cent NaOH calculated on the solution), and the boiling continued for five minutes. (*d*) The cellulose is now thrown upon a cloth filter, and washed with hot water. It will be found to be almost pure, *i.e.*, white; but to remove the last residues of the non-cellulose, it may be bleached by immersion in a dilute solution by hypochlorite (0·1 per cent NaOCl) for a few minutes, or treated with dilute permanganate solution (0·1 per cent $KMnO_4$). It is well washed from these oxidising solutions, treated with sulphurous acid on the filter, well washed with water, squeezed, dried, and weighed.

In another place these authors state that in applying this process to wood, it is necessary to reduce the wood "to the finest possible shavings." In giving directions for obtaining cellulose from pine wood (*loc. cit.*, p. 244) they say that after treating the finely divided wood as in the above quoted passage, the chlorination must be repeated until pure cellulose is obtained.

It is, of course, impossible to follow the directions given above when using finely ground wood, since the quantitative removal of such a material from a gauze or cloth filter, without the use of a stream of water, is practically impossible. After some experimenting we adopted the following method of procedure.

The wood was dried out at a low temperature, 60—80°, and ground in a hand mill. The material was then sifted through a sieve having twenty-four meshes to the inch. The wood powder obtained in this way was dried at 100—105°, and weighed portions of about 5 grms. each used for each determination. The sample, after being boiled in 200 cc. of 1 per cent sodium hydroxide solution for a half-hour, was filtered with suction on a small perforated porcelain plate in a five-inch funnel. In order to hold the plate firmly in the funnel during the filtration and the subsequent manipulation, we passed a piece of fairly stiff silver wire up through one of the holes in the centre of the plate and securely fastened it by bending the end down. The silver wire extended down through the stem of the funnel, projecting a quarter of an inch beyond the end. By putting one or two slight bends in the wire it can be made to bear against the walls of the inside of the stem, and the filter plate is held firmly in place. When the ground wood is first poured on to such a plate it behaves much like asbestos, some running through and the rest matting down and forming a coherent layer. The portions running through are then poured back, and by careful manipulation no significant loss of fibre occurs. The wood which had been boiled in alkali was washed on the filter with a large volume of water. The matted fibre was loosened up with a sharp pointed glass rod, and the rubber tube leading from a chlorine generator attached to the stem of the funnel. A slow stream of washed chlorine gas was passed up through the material, which was occasionally stirred to allow a thorough penetration of the gas.

After the chlorination the funnel was returned to the suction flask and the fibre washed to remove hydrochloric acid. For the boiling in sodium sulphite solution it was necessary to remove the material to a casserole. This may be readily accomplished by inverting the funnel over the casserole and pushing on the silver wire projecting

TABLE I.

Wood	Length of chlorination.	Appearance of cellulose.	Per cent of cellulose.	Per cent gain with ferrocyanide reaction.
Longleaf pine—Sapwood ..	2 chlorinations of 1 hour and ½ hour	Cream colour	53·5	
„ ..	4 „ of ½ hour each ..	White	53·8	
„ ..	2 „ „ „ ..	Light cream (uneven)	58·4	
Heartwood (*a*)	3 „ ⅔, ⅔, and ½ hour ..	White	45·8	
„ ..	3 „ „ „ ..	Light cream	49·0	
„ ..	3 „ „ „ ..	Dark	52·8	
Loblolly pine—Sapwood . ..	3 „ ½ hour each	Dark	60·8	
„ ..	2 „ „	Dark	63·3	
„ ..	3 „ ½ hour and 1 of ⅔ hr.	White	53·9	
„ ..	2 „ „ „	White	54·5	
Heartwood (*a*)	2 „ ⅔ hour and 1 of ½ hr.	Light cream	49·6	3·80
„ ..	3 „ ⅔ hour	Light cream	48·1	2·69
Lodgepole pine—Sapwood ..	2 „ „	Light cream	59·4	6·71
„ ..	2 „ „	Light cream	58·8	4·18
Heartwood .	3 „ ½ hour and 1 of ½ hr.	White	43·7	2·36
„ ..	3 „ „ „	Very white	40·4	4·05
„ ..	2 „ ½ hour	Cream colour	49·5	−0·59
„ ..	2 „ „	Cream colour	50·4	−3·77
Spruce—Mixed heart and sap.	2 „ ½ hour and 1 of ⅔ hr.	Light cream	59·6	3·94
„ „	2 „ ½ hour	Dark	63·8	6·07

(*a*) In boiling with Na_2SO_3 after the first chlorination of this sample, the solution was made alkaline to 0·4 per cent instead of the usual 0·2 per cent.

from the stem. The main mass of the material drops out and the remainder is readily washed from the funnel and filter plate with the aid of 150 cc. of 2 per cent sodium sulphite solution which has been previously measured into a wash-bottle. After bringing the sulphite solution to a boil, 3 cc. of a 10 per cent sodium hydroxide solution were added and the mixture boiled for five minutes. The fibre was again collected on the filter plate, washed with hot water until the washings were colourless, and the product again chlorinated, or, when desired, bleached in the funnel by the use of 0·1 per cent potassium permanganate solution followed by sulphurous acid. In order to conveniently weigh the final product it was transferred from the funnel to a beaker, with the aid of alcohol from a wash-bottle, and then collected in a large, tared Gooch crucible, dried, and weighed.

A single chlorination, even if prolonged for two hours, was insufficient to yield a white cellulose after permanganate bleaching. The greatest difficulty in the whole process lay in judging the end-point. Finely ground wood is not homogeneous, since there are always small pieces made up of cells from the summer wood of the annual rings, and these cells with their thick walls offer a marked resistance to reagents. It frequently happened that after a series of chlorinations and permanganate bleachings which reduced the great mass of the sample to white cellulose that there still remained particles which were yellow. Since treatment with chlorine gas will attack wood cellulose to some extent, it became questionable whether or not continued chlorination did not cause a loss of cellulose in the finer particles which introduced a greater error than that caused by stopping the treatment before the sample was uniformly white.

The lignocelluloses when immersed in a mixture of equivalent solutions of potassium ferricyanide and ferric chloride are stained blue with the fixation of both iron and cyanide groups. The gain in weight occurring in this reaction varies with the quantity of ferric ferricyanide solution which is used. Sherman found that with the same volumes and strengths of solutions, and the same time of immersion, the gain in weight was constant for a given sample. By applying the reaction to the cellulose obtained by the different methods, he obtained a criterion of their purity. Of the use of the reaction he says (*loc. cit.*, p. 304), "The reaction with the ferricyanide solution seems of considerable value in testing the purity of celluloses. When the sample increases only slightly (about 1 per cent or less) in weight and is dyed only a bluish-green instead of a deep blue colour, it is at least a very strong indication that lignin substances are not present in notable quantity."

In applying this reaction to the products obtained by us, we have followed Sherman's procedure:—10 cc. of 1·6 per cent solution of ferric chloride were mixed with 10 cc. of a freshly prepared 3·3 per cent solution of potassium ferricyanide; to this mixture 1 grm. of dry material was added, and after standing one hour, with occasional stirring, the dyed fibre was collected on a Gooch filter, washed with water, dried, and weighed. In some cases the filtrate from the fibre was a deep green instead of the brownish-red colour of the ferric ferricyanide solution, and it happened in a number of cases that a loss of weight followed the treatment, showing that soluble products were formed by the action of the ferricyanide solution on some of the constituents of the cellulose.

The results of the first series of estimations are given in Table I. After weighing out the samples of the more resinous woods, they were extracted with ether before the alkaline boiling.

The results which are summarised in Table I. show that the chlorination method is not easily controlled for quantitative estimations. In estimations of this sort it is not to be expected that the results will be concordant to small fractions of a per cent, but the variations observed seem rather too large even for proximate analyses. As stated above, the difficulty of judging the end-point of the process was very great. The same treatment did not always yield the same kind of a product nor show the same percentage of cellulose. If the chlorinations were continued until a perfectly white product was obtained, the percentages were not always alike and seemed to be too low. The results of the ferricyanide reaction did not appear to be of much help.

To assist in clearing up some of these points, we have carried out a series of systematic determinations on four different kinds of wood. Of each kind of wood four (five in the case of No. 1) samples of about five grms. were taken. The first sample was boiled in alkaline solution as described above, chlorinated once for one hour, boiled in sulphite solution, treated with permanganate and sulphurous acid, washed, and dried; the next sample was treated in precisely the same way except that it had two one-hour chlorinations and the accompanying sulphite boilings; and so on, each sample receiving one more

chlorination than the one before it. In the case of Wood No. 1 the final washings were carried out in the funnel, as in the former experiments, with the other woods the final product was boiled for five minutes in a large volume of distilled water in order to ensure the removal of all reagents. The different kinds of wood, and each of the celluloses, were tested by the ferricyanide reaction. The results are summarised in Table II.

TABLE II.

		Colour.	Per cent of cellulose.	Per cent gain by ferricyanide reaction.
Wood No. 1: Heartwood of Red Spruce.				
Wood..		—	—	13·85
Cellulose by chlorination	1	Light brown	61·9	2·52
,, ,,	2	Light cream	58·5	0·11
,, ,,	3	White. ..	51·9	−1·50
,, ,,	4	White. ..	49·1	−1·55
,, ,,	5	White. ..	46·8	−1·42
Wood No. 2: Sapwood of Red Spruce.				
Wood..		—	—	9·51
Cellulose by chlorination	1	Light brown	63·5	6·69
,, ,,	2	Light cream	53·5	0·79
,, ,,	3	White. ..	51·3	−1·56
,, ,,	4	White. ..	47·9	−2·83
Wood No. 3: Heartwood of Balsam Fir.				
Wood..		—	—	11·63
Cellulose by chlorination	1	Light brown	57·3	4·2
,, ,,	2	Cream. ..	49·4	2·54
,, ,,	3	White. ..	44·1	2·02
,, ,,	4	White. ..	44·6	1·75
Wood No. 4: Sapwood of Lodgepole Pine.				
Wood..		—	—	7·77
Cellulose by chlorination	1	Dark cream	54·6	1·36
,, ,,	2	Light cream	54·3	1·40
,, ,,	3	White. ..	52·3	0·87
,, ,,	4	White. ..	49·1	−0·10

None of the woods here are very resistant, and in only one case, Balsam Fir, was trouble given by the presence of refractory particles which would not become perfectly white. In all cases when the fibre had received two chlorinations of one hour each, it bleached when again subjected to the action of chlorine gas, instead of turning to the orange-red characteristic of lignocelluloses. Cross and Bevan believe that this orange colour with chlorine is a *characteristic* reaction. If that be true, then the complete removal of the lignone complex must take place early during the third chlorination, and the percentage of cellulose falls in between the values found with two and with three chlorinations. The ferricyanide reaction fails to give wholly satisfactory results. We have never been able to obtain a cellulose from wood which does not give a blue-green colour with this reagent. Why the deep green filtrates should be obtained from some of the tests, and a loss of weight should occur, is not apparent.

The final working out of the following satisfactory analytical procedure was greatly aided by the realisation that the end-point was indicated by the bleaching of the cellulose in chlorine, and by finding that satisfactory samples could be secured by the use of a wood-worker's rasp.

By holding the wood to be sampled in a vice, and rasping lightly, a finely fibrous sample is readily obtained. The best samples are prepared from green wood; when dry wood is to be sampled, it should be soaked or boiled until thoroughly softened before being rasped. The material is brought to an air-dry condition, any large pieces which may perchance be present picked out with forceps, and the very fine particles removed by shaking the air-dry sample on cheese cloth or a very fine sieve. The resulting uniform material is then dried at 98—100°, and 5 grm. portions used for analysis.

The first chlorination should be for one hour; the length of subsequent chlorinations must be to some extent a matter of judgment. If the fibre takes on a very deep orange, showing that a large amount of the lignone is still present, the second chlorination should be for a half or even three-quarters of an hour; if lighter colours appear, the time should be shorter. The wood of deciduous trees gives a far paler orange colour with chlorine than that of the coniferous species, and more readily yields a pure cellulose.

The rate of chlorine flow influences the length of exposure required. This is brought out in analyses 1 to 4 in Table III. In analyses 1 and 2 the chlorine was passed in slowly, the first chlorination was not complete, and a second treatment was required. In analysis 3, the gas was passed in more rapidly, and when the fibre was exposed to chlorine the second time it bleached at once. The final result is not influenced, provided the fibre is removed immediately after bleaching occurs. If the cellulose is not removed from the action of chlorine as soon as bleached, it is attacked and a significant loss occurs, as shown in analysis No. 4. When bleaching occurs, the funnel should be transferred to the filter flask, the cellulose treated with water containing a little sodium bisulphite to act as an "anti-chlor," then thoroughly washed, transferred to a large size Gooch crucible, and finally washed in the crucible with alcohol and ether. The first part of the drying should be at a gentle heat, ending with a temperature of 98—100°.

Several analyses are given in Table III., all of them satisfactory, except No. 4, where the chlorine was allowed to act on the bleached cellulose.

TABLE III.

No.	Material.	Chlorinations.	Per cent of cellulose.
1.	White oak—Sapwood ..	1 hour, 20 minutes, and to bleach ..	55·90
2.	,, ,, ..	Do. Do. ..	56·34
3.	,, ,, ..	1 hour and to bleach	56·40
4.	,, ,, ..	Do. Do.	54·79
5.	Red cedar—Sapwood ..	1 hour, 30 minutes, and to bleach ..	42·04
6.	,, ,, ..	Do. Do. ..	41·51
7.	,, Heartwood.	Do. Do. ..	42·52
8.	,, ,, ..	Do. Do. ..	43·00
9.	Red spruce—Heartwood	1 hour, 10 minutes, and to bleach ..	58·95
10.	,, ,, ..	Do. Do. ..	58·60
11.	Cherry—Sapwood . ..	1 hour and to bleach	54·72
12.	,, ,, . ..	Do. Do. ..	54·43

The final products were all pure white, and none of them gave the lignin reaction with phloroglucinol and hydrochloric acid.

In conclusion, we desire to acknowledge our indebtedness to Mr. D. C. Parmelee for valuable assistance given us in the analytical work.—*Journal of the American Chemical Society*, xxix., No. 7.

Lothar Meyer Memorial.—As lately announced by Sir William Ramsay, Professor Wislicenus (of Tübingen) is arranging the establishment of a memorial to the late Professor Lothar Meyer. The Treasurer of the Chemical Society is prepared to receive donations towards the fund, and contributors are therefore requested to forward their subscriptions to him, in envelopes endorsed "Lothar Meyer Memorial," at Burlington House, W.

POTASSIUM AMMONOZINCATE.

A Representative of a New Class of Compounds.

By EDWARD C. FRANKLIN.

Following the programme of developing the ammonia system of acids, bases, and salts inaugurated in the Stamford University laboratory, Mr. F. F. Fitzgerald (*J. Am. Chem. Soc.*, xxix., 656) has succeeded in preparing an ammonia analogue of the potassium zincate which is generally (Abegg's "Handb. Anorg. Chem," ii., 338) assumed to be formed when metallic zinc, zinc oxide, or zinc hydroxide is dissolved in an aqueous solution of potassium hydroxide. He obtained this ammono salt, to which he gave the formula $Zn(NHK)_2.2NH_3$, by the action of an ammonia solution of potassium amide on metallic zinc and on zinc amide in accordance with the equations $Zn + 2KNH_2 + Am = Zn(NHK)_2.2NH_3 + H_2$, $Zn(NH_2)_2 + 2KNH_2 = Zn(NHK)_2.2NH_3$, which are obviously analogous to the reactions whereby Comey and Jackson (*Am. Chem. Journ.*, xi., 145) prepared the compounds $Zn_3O_6Na_4H_2.19H_2O$ and $(ZnO_2NaH)_2.7H_2O$, and Förster and Gunther (*Zeit. Elektrochem.*, vi., 301) the compound to which they gave the formula $(OH)Zn(ONa).3H_2O$. (This latter compound, it should be noted, is probably identical with the compound $(ZnO_2NaH)_2.7H_2O$, of Comey and Jackson, inasmuch as the two products differ in composition by half a molecule of water only.)

Unfortunately Fitzgerald's work was brought to a sudden end by the great earthquake before entirely satisfactory evidence as to the composition of his product had been procured. In view of the importance of establishing definitely the existence of a compound belonging to this group of the ammonia system, the writer has continued Mr. Fitzgerald's work and has succeeded in preparing a beautifully crystallised compound, the analytical data for which point sharply to the formula $Zn(NHK)_2.2NH_3$, or $Zn(NH_2)_2.2KNH_2$, thus confirming the earlier results.

Preparation of Potassium Ammonozincate.

The pure compound has been prepared by the action of an excess of potassium amide in solution in liquid ammonia on pure, water-free, ammoniated zinc iodide in accordance with the equation $ZnI_2.4NH_3 + 4KNH_2 = Zn(NHK)_2.2NH_3 + 2KI + 2NH_3$. The manipulative details were carried out as follows, using the form of apparatus and methods of procedure previously described (*Journ. Am. Chem. Soc.*, xxvii., 830) by the writer. Clean metallic potassium, together with a few milligrms. of platinum black, were introduced into one leg of the apparatus, after which this leg was closed before the blowpipe. Into the other leg was then introduced the zinc salt, which was melted in a current of ammonia gas to a perfectly clear, colourless liquid, after which the tube was sealed as usual. As soon as the conversion of the metallic potassium into potassium amide was complete, the solution of the latter was poured in excess into the leg containing the zinc iodide. Zinc iodide is soluble as such to a limited extent only. Addition of a small quantity of potassium amide greatly increases the solubility of the zinc salt, a behaviour for which the explanation is not obvious. Increasing the amount of potassium amide finally produces a permanent flocculent precipitate which, in the presence of an excess of the precipitant, gradually, in the course of some hours, changes into a mass of dense, colourless, well formed crystals. After washing a few times the salt is obtained pure.

Method of Analysis.

For analysis the tube containing the pure salt was separated from the remainder of the apparatus and evacuated of its gaseous contents by means of a mercury pump at laboratory temperature. The tube was weighed, delivered of its contents, evacuated and weighed again, thus giving the weight of the salt which during this process has at no time been in contact with the air or other source of contamination with water. The substance in solution in dilute hydrochloric acid is divided into aliquot parts, in one of which the nitrogen is determined by distillation with potassium hydroxide and titration of the distillate after the usual volumetric method for ammonia. In another portion of the solution the zinc is precipitated by the addition, in excess, of a measured amount of a standard solution of sodium carbonate, followed by digestion on the water-bath until the ammonia is entirely removed and the precipitation of the zinc is complete. The filtrate from the zinc carbonate is acidified with hydrochloric acid, evaporated to dryness and ignited, thus giving a mixture of known sodium chloride content.

Analytical Data.

The following analytical results have been obtained:—

Preparation I. One-fourth of 0·5962 grm. of the substance gave 0·0398 grm. nitrogen; another fourth gave 0·0586 grm. zinc oxide.

Preparation II. One-half of 0·6858 grm. of this preparation gave 0·093c grm. nitrogen; the other half gave 0·1367 grm. zinc oxide and 0·2446 grm. potassium chloride.

Preparation III. One-half of 0·7424 grm. of the substance gave 0·1008 grm. nitrogen; one-fourth of 0·7424 grm. of the substance gave 0·0727 grm. zinc oxide and 0·1338 grm. potassium chloride.

From these results the following percentages of the respective constituents have been calculated:—

	Calculated for $Zn(NHK)_2.2NH_3$.	Found. I.	Found. II.	Found. III.
N	27·04	26·7	27·1	27·1
Zn . ..	31·44	31·5	31·9	31·4
K	37·70	—	37·5	37·7

It should be mentioned here that the discrepancies in the analytical data obtained by Fitzgerald were undoubtedly caused by the presence of water, very small quantities of which, acting hydrolytically on the ammono salt, set free ammonia and form the hydroxides of zinc and potassium.

It is of further interest in this connection to note that the writer, in his attempts to prepare, filter, and wash this compound in a piece of apparatus devised for working with liquid ammonia solutions at atmospheric pressure, always obtained products which were low in ammonia and high in potassium and zinc, the results, as he believes, of his inability to exclude all traces of moisture when working with such a cold liquid as ammonia is at low pressures. The moisture probably finds its entrance past the numerous stoppers and stop-cocks used.

Properties of the Salt.

Potassium ammonozincate is but slightly soluble in liquid ammonia, but is dissolved energetically and with the evolution of much heat in dilute aqueous acids. It is also soluble in liquid ammonia solutions of ammonium salts. It is very susceptible to the action of water, which converts it into ammonia, zinc hydroxide, and potassium hydroxide; even very short exposure to the action of the moisture of the air produces a superficial, sticky layer on the clean, dry crystals. It is not explosive. When heated *in vacuo*, potassium ammonozincate remains unaffected up to about 160°. As the temperature is increased the substance melts and gives off ammonia. One specimen heated to 250° for some hours until the evolution of ammonia had practically ceased, gave off 11·3 per cent of ammonia and yielded a dark, varicoloured residue which gave on analysis 18·7 per cent nitrogen, 36·8 per cent zinc, and 44·7 per cent potassium. Another specimen heated to 300° for a considerable time lost 11·6 per cent ammonia and gave a residue containing 18·8 per cent nitrogen. The evolution of one and a-half molecules of ammonia from $Zn(NHK)_2.2NH_3$ would require a loss of 12·3 per

cent in weight, while a compound of the composition $Zn(NHK)_2.\frac{1}{4}NH_3$, would contain 19·2 per cent nitrogen, 35·8 per cent zinc, and 43·1 per cent potassium. As the temperature is raised ammonia mixed with permanent gases is given off, and at the same time rings of metallic potassium and zinc are deposited in the cooler end of the tube. When a third specimen was heated to 325° for many hours it lost 14·8 per cent of its weight, apparently showing that even at this temperature all the ammonia of crystallisation is not driven off. On emptying the tubes after heating these preparations to 250° and higher, the glass walls of the tubes were found to be much attacked by the melted salt, a fact which accounts for the divergent analytical results, and at the same time discouraged any further attempts to obtain a definite compound by the elimination of ammonia from the compound $Zn(NHK)_2.2NH_3$. In one experiment a tube lined with platinum was used in the hope that definite results might thus be obtained, but it was found that the melted salt also attacked this metal. It should be pointed out, however, that the results obtained point to the probable existence of a compound of the formula $Zn(NHK)_2.\frac{1}{4}NH_3$.

Summary.

It is shown by the work described above that a potassium ammonozincate, an ammonia analogue of the hypothetical water salt, potassium zincate, is obtained in the form of a definite, well crystallised compound by the action of a liquid ammonia solution of potassium amide, first on metallic zinc, second on zinc amide, and third on zinc iodide, in accordance with the following respective equations:—

1. $Zn + 2KNH_2 + Am. = Zn(NHK)_2.2NH_3 + H_2$,
2. $Zn(NH_2)_2 + 2KNH_2 = Zn(NHK)_2.2NH_3$,
3. $ZnI_2.4NH_3 + 4KNH_2 = Zn(NHK)_2.2NH_3 + 2KI + Am.$

—*Journal of the American Chemical Society*, xxix., No. 9.

THE ACTION OF HYDROCHLORIC ACID ON MANGANESE DIOXIDE.

(PRELIMINARY PAPER).

By WILLIS B. HOLMES.

A GREAT deal of work has been done upon the interaction of hydrochloric acid and manganese dioxide. Although the bulk of experimental evidence seems to point to the probable formation of the trichloride and tetrachloride of manganese, a final decision in this case has not yet been reached. None of the intermediate products of the reaction have ever been isolated, and the experimental work bearing upon this subject is of an indirect nature. Two general methods of attacking this problem have been in vogue; the treatment of manganese dioxide with an ethereal solution or with an aqueous solution of hydrogen chloride and the subsequent analyses of the solutions thus obtained. The former method excludes the presence of water, except such as is formed by the reaction itself, while the latter method introduces it.

Manganese Dioxide Treated with an Ethereal Solution of Hydrogen Chloride.—Nicklès (*Ann. Chem.*, 41, v., 161) treated manganese dioxide with an ethereal solution of hydrogen chloride, and obtained a dark green solution, the colour of which, on further dilution with ether, changed to a deep violet. On saturating this solution with hydrogen chloride he obtained a green oil which he claimed contained manganese tetrachloride. One analysis gave results for $MnCl_4.12(C_2H_5)_2O.2H_2O$. Nicklès' results, however, are not conclusive.

Christiansen (*Journ. Prakt. Chem.*, xxxiv., 41, and xxxv., 57) suspended manganese dioxide in ether, saturated the ether with chlorine, and obtained a violet solution. By decanting this violet solution, he obtained a black residue which also partly dissolved in ether and gave the same violet colour to the solution. (This black residue is of interest, as it probably contained some manganese trichloride). He then treated manganese dioxide with ether which had been saturated with hydrogen chloride, and obtained a green solution. He considered that the violet solution and the green solution both contained the same dissolved substance, the difference in colour being due to the presence of water in the former case. For analysis a portion of the green solution was run into a solution of potassium iodine and the liberated iodide titrated with a solution of sodium thiosulphate. From these results the available chlorine was estimated. (The term available chlorine refers to the chlorine in excess of that required for manganous chloride). The total manganese in this solution was then determined. The average ratio of total manganese to available chlorine from seven analyses was 1 : 1·06. He thus concluded that manganese trichloride was formed in both cases. By working at a temperature of about −10° he obtained a higher ratio—approximately, 1 : 1·5—and thought that the tetrachloride might be formed at lower temperatures.

Franke (*Journ. Prakt. Chem.*, xxxvi., 31 and 451) repeated Christiansen's work, and obtained the same ratio of manganese to available chlorine, approximately 1 : 1, but interpreted the results differently. He thought that hydrogen chloride, instead of water, caused the difference between the blue and green solutions; that the green solution with the excess of hydrogen chloride contained chloromanganic acid, while the violet solution contained manganese tetrachloride. Manganous chloride was always present as a decomposition product, and united with the chloromanganic acid forming manganous chloromanganate,

$$MnO_2 + 6HCl \rightarrow H_2MnCl_6 + 2H_2O,$$
$$MnCl_2 + H_2MnCl_6 \rightarrow MnMnCl_6 + 2HCl.$$

The green solution on further dilution with ether separated into manganous chloride and manganese tetrachloride, the violet colour becoming evident as the tetrachloride was extracted. The ratio 1 : 1 was thus interpreted. His analysis of the violet solution gave the ratio of total manganese to available chlorine from 1 : 1·68 to 1 : 2·35. This ratio indicated the presence of the tetrachloride. The violet solution treated with a little water gave a precipitate of hydrated manganese dioxide.

Manganese Dioxide Treated with an Aqueous Solution of Hydrogen Chloride.—Fisher (*Journ. Chem. Soc.*, xxxiii., 409) treated manganese dioxide with strong hydrochloric acid in the proportion of one part of the dioxide to ten parts of the acid. The resultant solution was filtered through spun glass and run into a burette. A known volume was then delivered into a solution of potassium iodide, and the iodine titrated in the usual way. An equal volume was then run into a solution of sodium acetate, and the precipitated manganese was separated, ignited, and weighed as mangano manganic oxide. The filtrate was then treated with potassium iodide, and the free chlorine estimated. This, subtracted from the result in the first solution, gave the available chlorine. The ratio of precipitated manganese to available chlorine was approximately 1 : 2, and hence the conclusion that the tetrachloride was formed. He assumed that the precipitated manganese was entirely a hydrated dioxide, and that the tetrachloride, in the presence of hydrochloric acid, existed in a form analogous to chloroplatinic acid.

Pickering (*Journ. Chem. Soc.*, xxxv., 654) repeated Fisher's work and obtained different results. His general method of procedure was the same, except that he used water instead of a solution of sodium acetate, and analysed his precipitated manganese by a method whereby he could estimate not only the total manganese, but also the amount of dioxide which it contained. His results showed that the precipitated manganese was not entirely a dioxide but a mixture of different oxides; that the ratio of total manganese to available chlorine was nearly 1 : 1·64, and that the ratio of manganese dioxide to available chlorine

was 1 : 2. He concluded that the reaction took place as follows :—

$$\text{I. } 2MnO_2 + 8HCl \rightarrow Mn_2Cl_6 + Cl + 4H_2O,$$
$$\text{II. } Mn_2Cl_6 + 2H_2O \rightarrow MnO_2 + MnCl_2 + 4HCl,$$

because he was never able to obtain more than half of the manganese as a precipitate. If Equation II. was correct then the amount of precipitated manganese should increase if the experiment was performed in the presence of manganous chloride, whereas the amount should remain stationary if the tetrachloride was formed. The amount of precipitated manganese did increase when manganous chloride was added to the solution, which indicated the presence of the trichloride. The effect of temperature upon the amount of manganese precipitated also indicated the formation of the trichloride. If the substance was a tetrachloride, at low temperatures, 100 per cent should be precipitated, and in the case of the trichloride only 50 per cent. At 60°, less than 10 per cent was precipitated, and at low temperatures the amount approached 50 per cent.

Vernon studied the action of hydrochloric acid on manganese dioxide by estimating, at various temperatures, the rate of evolution of chlorine (*Phil. Mag.*, lxxxi., 469, and CHEMICAL NEWS, lxi., 203). If Pickering's view is correct,—

$$2MnO_2 + 8HCl \rightarrow Mn_2Cl_6 + Cl_2 + 4H_2O,$$

then half of the available chlorine ought to be evolved very rapidly. This was not found to be the case, especially at low temperatures. From the result of his experimental work, Vernon concluded that manganese tetrachloride is always the first product formed when manganese dioxide is dissolved in hydrochloric acid.

Wacher (*Chem. Zeitung.*, xxiv., 285) dissolved manganese dioxide in concentrated hydrochloric acid, and obtained a brown solution which, on dilution with water, gave a precipitate of hydrated manganese dioxide. He then passed chlorine into a solution of manganous chloride in concentrated hydrochloric acid, and obtained a similar brown solution. This solution also gave a precipitate of hydrated manganese dioxide when diluted with water. From these results he concluded that the tetrachloride of manganese was formed, but gave no experimental evidence to show that the precipitate was entirely hydrated manganese dioxide.

Double Salts.—Numerous double chlorides containing manganese trichloride and tetrachloride have been isolated. Rice (*Journ. Chem. Soc.*, lxxiii., 258) and Newman (*Monatsh.*, xv., 489) obtained the double chlorides, $2KCl.MnCl_3$ and $2NH_4.MnCl_3$. Meyer and Best (*Zeit. Anorg. Chem.*, xxii., 169) obtained similar double salts with quinoline and pyridine hydrochloride $MnCl_3.2C_9H_7NHCl$ and $MnCl_3.2C_5H_5NHCl$. They also obtained the double chlorides, $2CsCl.MnCl_3$, $MnCl_4.2KCl$, and $MnCl_4.MnCl_3.5KCl$. Reitzenstein obtained a dipyridine manganese tetrachloride (*Zeit. Anorg. Chem.*, xviii., 290).

Experimental Part.

Previous failures to isolate the intermediate products of the interaction of hydrochloric acid and manganese dioxide probably depend upon the fact that such products are decomposed by water and heat. The reaction itself liberates water, but it seemed possible by reducing the amount of water to a minimum and at the same time keeping the temperature low, to obtain some information concerning the nature of the products formed. This proved to be the case.

The method of treating manganese dioxide with a solution of hydrogen chloride in absolute ether was not found practical. While the ratio of precipitated manganese to available chlorine could be determined from such a solution, the total chlorine could not be estimated, as it was impossible to get rid of the excess of hydrogen chloride. Attempts to precipitate the product soluble in the ethereal solution by adding a large excess of carbon disulphide or toluene, proved unavailing. A green oily liquid could be obtained, but it was impossible to do anything with it. Some medium was then sought for which would not dissolve any of the compounds of manganese formed and at the same time would dissolve hydrogen chloride and not be affected by it, or by any of the decomposition products of the reaction. Carbon tetrachloride seemed to fulfil the necessary conditions, and was used throughout for the preparation of material.

The following method of procedure was followed. Five grms. of precipitated manganese dioxide was mixed with 200 cc. of carbon tetrachloride, and put in a long-necked 500 cc. vacuum flask. This flask was then inserted in a shaking machine. The shaking machine was made of a board 40 × 15 cm., with a hole in the middle for the insertion of the neck of the flask, and supported at each end by a 30 cm. upright. The neck of the flask was held in place by a perforated rubber stopper. A short shank extending from the side of the board was connected with an eccentric on wheel run by a small motor. This gave a lateral motion to the flask, which was inserted in a pneumatic trough filled with finely-ground ice and water. The shaking served the double purpose of keeping the flask and its contents cold and of agitating the mixture. Dry hydrogen chloride was then bubbled through the carbon tetrachloride. As water was formed during the reaction, no extreme precautions were taken to dry the gas, although it was passed through several towers filled with beads and sulphuric acid. Hydrogen chloride is not extremely soluble in carbon tetrachloride, so the gas was allowed to bubble through for an hour and a-half. The reaction was then practically complete, and the solid residue in the flask was separated by filtration.

The filtrate of carbon tetrachloride gave no test for manganese, but was coloured yellow from the dissolved chlorine. A large amount of chlorine was always formed, and could even be detected in the wash-bottle used to absorb the unused hydrogen chloride.

The solid residue consisted of a greenish black substance, which on standing slowly decomposed with the evolution of chlorine and hydrogen chloride. When it was dried in a desiccator with potassium hydroxide and sulphuric acid, decomposition set in, and a substance of a reddish brown colour remained; but when dried quickly by means of filter-paper and warmed, it gave off chlorine and hydrogen chloride. A little put in a large amount of water gave an immediate precipitate, probably hydrated manganese dioxide. Treated with absolute ether, it gave a solution of an intense violet colour. On standing, this solution gradually lost its violet colour, and manganous chloride separated out; but if kept cold the solution retained its colour from twelve to forty-eight hours. If hydrogen chloride was passed into this violet solution, it turned green. On continued washing of the original residue with ether the compound which imparted the violet colour was entirely dissolved out, and a reddish brown residue remained. This substance, which dissolved in ether with the formation of a violet solution, proved to be manganese trichloride.

The reddish brown residue was much more stable than the original residue. It could be kept in a desiccator for a long time without undergoing any appreciable decomposition, but decomposed immediately on exposure to moist air. When warmed it gave off chlorine, and left a residue of manganous chloride. It dissolved in absolute alcohol forming a solution of deep wine colour which slowly decolorised on standing. This substance proved to be manganese tetrachloride. About one-half of the original residue was manganese trichloride, the remainder being a mixture of manganous chloride and manganese tetrachloride.

Manganese Trichloride.—The analysis of this substance offered many difficulties. The solid could not be prepared in a condition pure enough for analysis. Attempts to obtain the trichloride from the ethereal solution by evaporating the ether by means of a current of dry cold air proved unavailing, as decomposition always set in. The analysis of the ethereal solution was then attempted. In preparing this solution for analysis the utmost care was

necessary. It was very difficult to remove the last traces of hydrogen chloride, and all reagents used had to be anhydrous and kept at a low temperature. The work had to be performed as expeditiously as possible, and a dilute solution used in order to prevent decomposition.

The residue of mixed chlorides from the flask was first washed with a large amount of carbon tetrachloride. This removed part of the hydrogen chloride. It was next washed with carbon disulphide to remove the carbon tetrachloride, and then transferred to a flask containing carbon disulphide, to which a little ether had been added, and shaken. This treatment seemed to be the most effective method of removing the last traces of the hydrogen chloride, and was repeated a second time. The residue was then transferred to a funnel and washed with ether, which had been cooled with solid carbon dioxide, until about two-thirds of the trichloride had been removed. The filter-paper and residue were then put in a special funnel connected with a litre filtering flask. The funnel was surrounded with a jacket so that it could be kept cold by means of ether and solid carbon dioxide. The flask held 250 cc. of ether, and was placed in a mixture of ice and salt. The residue was then washed with about 100 cc. of the cold ether, and this solution, diluted with the ether in the flask, was used for analysis.

In the analysis, three quantities were estimated; the available chlorine, the total chlorine, and the total manganese. In certain cases the precipitated manganese was also obtained. A 50 cc. pipette, protected by a drying tube, was used to run off equal portions of the solution into six receptacles. The first four consisted of litre filtering flasks fitted with rubber stoppers, and carrying glass tubes large enough for the insertion of the pipette. One and two each contained about 300 cc. of a dilute solution of potassium iodide, and were used to estimate the available chlorine. Three and four each contained about 300 cc. of a dilute solution of silver nitrate to which a little nitric acid had been added, and were used to estimate the total chlorine. The arms of the flask were connected with U-tubes containing the same solutions, and these in turn were connected with an aspirator. Air was aspirated through each flask during the filling. The contents of the tubes were afterwards added to the flasks. Five and six were beakers each containing about 200 cc. of water, and were used to determine the total manganese.

The iodine was titrated with a one-tenth normal solution of sodium thiosulphate, and from the results obtained the available chlorine was estimated. The silver chloride was determined by the regular crucible method, and the total chlorine estimated. Only a part of the manganese was precipitated, so ammonium hydroxide and bromine water were added to the solution to precipitate all the manganese. The precipitate was then filtered, washed, ignited in a Rose crucible, and weighed as mangano-manganic oxide. It was then converted into manganous sulphide, and weighed again. When the quantity of manganese was very small, the oxide and sulphide methods gave identical results, but with larger amounts there was a slight variation. The sulphide results were used throughout as being the more reliable.

Analysis I.—This analysis was a preliminary one performed to get some idea of the ratio between the available chlorine and the total chlorine. It gave results as follows:—

Available chlorine (grm.) ..	0·0198	0·0198
Total chlorine (grm.)	0·0618	—

Ratio of available chlorine to total chlorine, 1 : 3·12.

Analysis II.—This analysis was performed before it was realised that the manganese trichloride retained some hydrogen chloride. The results are inserted, however, as they give an indication of the amount of hydrogen chloride retained. The residue was only washed with enough carbon disulphide to insure the complete removal of the carbon tetrachloride, and the ethereal solution was then prepared. This washing removed some of the hydrogen chloride, but enough remained to give an indication of the probable amount retained. Two additional portions of the ethereal solution were run into two beakers, each containing 300 cc. of water, and the filtrates were examined as follows:—The first was tested for free chlorine with a negative result, and the second for manganese which had not been precipitated.

Available chlorine (grm.) ..	0·0212	0·0212
Total chlorine (grm.)	0·0758	0·0757
Total manganese (grm.) ..	0·0346	0·0343
Manganese in filtrate (grm)...	—	0·0168

0·0344 grm. of manganese requires 0·0665 grm. chlorine for the trichloride. Excess of chlorine 0·0093 grm., equivalent to 0·0096 grm. HCl. 0·1009 grm. $MnCl_3$ requires 0·0228 grm. HCl for the double chloride $MnCl_3HCl$. The above results suggest the double chloride $2MnCl_3.HCl$, but are indicative only and need further confirmation. The ratio of available chlorine to the calculated total chlorine is 1 : 3·13.

Analysis III.—The solution for this analysis was made with all possible precautions, but was a little too concentrated, and a slight decomposition was observed. Two additional portions of the ethereal solution were used to determine the ratio between the precipitated manganese and the manganese in the filtrate. These portions were each run into 500 cc. of water and immediately filtered.

Available chlorine (grm.) ..	0·0209	0·0209
Total chlorine (grm.)	0·0684	0·0684
Total manganese (grm.) ..	0·0348	0·0346
Precipitated manganese (grm.)	0·0167	0·0167
Manganese in filtrate (grm.)..	0·0183	0·0179

Theoretical ratio. Mn/Cl_3 = 0·517. Found, 0·507.

0·0347 grm. of manganese should require 0·0671 grm. of chlorine for the trichloride.

Ratio of available chlorine to total chlorine, 1 : 327.

Ratio of precipitated manganese to manganese in the filtrate, 1 : 1·08.

Analysis IV.—This analysis was made to determine the ratio between the total manganese and the total chlorine. Precautions were taken to wash the residue very carefully, and use a very dilute solution to insure a minimum of decomposition.

Total chlorine (grm.)	0·0319	0·0320
Total manganese (grm.) ..	0·0164	0·0165

Theoretical ratio, Mn/Cl_3 = 0·517. Found, 0·515.

Properties of the Trichloride.—Manganese trichloride is a solid almost black in colour, with a slight greenish tinge. Heat breaks it up, with the evolution of chlorine, and it is immediately decomposed by water. Absolute ether is the best solvent yet found for the trichloride. When allowed to stand in a desiccator it decomposes into manganous chloride and manganese tetrachloride. All samples thus treated gave the reddish-brown substance characteristic of the tetrachloride. The trichloride dissolves in absolute alcohol, giving a wine-coloured solution which answered all tests for the tetrachloride. A small amount of this wine-coloured solution, treated with a large amount of absolute ether and kept cold, soon assumed the violet colour characteristic of the trichloride. It is thus possible to pass from one chloride to the other and back again. This, together with the fact that only half of the manganese is precipitated when the ethereal solution is run into water, indicates that the breaking down of the trichloride takes place in two stages, as Pickering observed (*Journ. Chem. Soc.*, xxxv., 654).

I. $Mn_2Cl_6 \rightarrow MnCl_2 + MnCl_4$.

II. $MnCl_4 + 2H_2O \rightarrow MnO_2 + 4HCl$.

The composition of the precipitate has not yet been determined. This will be done, however, when the quantitative study of this reaction is taken up.

Manganese Tetrachloride.—The tetrachloride was prepared by treating manganese dioxide, suspended in carbon tetrachloride, with hydrogen chloride. The same method of procedure as was used in preparing the trichloride was followed, and the same precautions observed. The residue

was washed with absolute ether to remove the trichloride. Persistent washing with ether failed to remove the last traces of the trichloride, so the residue was dried by means of filter-paper and put in a desiccator to allow the remaining trichloride to decompose. This failure to remove the last traces of the trichloride was probably due to the slight decomposition of the tetrachloride when some halogen absorbent was present. Samples of the tetrachloride when first suspended in ether gave no coloration, but the ether soon assumed the violet colour of the trichloride. Attempts to prepare pure manganese tetrachloride by the above method proved unavailing, as manganous chloride was always formed. Absolute alcohol was the only solvent found in which the tetrachloride was soluble, and such a solution was analysed. Manganese chloride is soluble in absolute alcohol, so the amount present had also to be determined.

The solution for analysis was prepared in the following way:—The residue, after standing in the desiccator, was transferred to the funnel of the special filtering flask previously described. The funnel was kept cold by means of ether and solid carbon dioxide. The flask held 250 cc. of absolute alcohol, and was surrounded with a mixture of ice and salt. About 100 cc. of absolute alcohol, which had been cooled with solid carbon dioxide, was then filtered through this funnel. Four portions of the resultant solution were then pipetted off and run into the same flasks as were used with the trichloride for the estimation of available and total chlorine. Two additional portions were run into two beakers, each holding 500 cc. of water, and the precipitated manganese then determined. This result gave the amount of manganese contained in the tetrachloride. The filtrate contained manganous chloride, and this manganese was then precipitated and estimated. The sum of the two gave the total manganese. In the analysis one precaution had to be observed. The precipitated manganese dioxide and alcohol interact unless the precipitation is made in a large volume of water and the filtration performed immediately.

Analysis I.—In this analysis the manganese was precipitated in 300 cc. of water, and the filtration was delayed for a short time. The results, consequently, are a little irregular.

Analysis II.—In this analysis the manganese was precipitated in 500 cc. of water and the filtration performed immediately.

Properties of the Tetrachloride.—This chloride is a solid of reddish brown colour, stable at ordinary temperature, if kept dry, but it quickly decomposes on exposure to moist air. Samples have been kept for several weeks in a desiccator without undergoing appreciable decomposition. But in a large amount of water the tetrachloride gives an immediate precipitate, probably hydrated manganese dioxide. Heated to 100° it gives off chlorine, and a residue of manganous chloride remains. When the tetrachloride is suspended in ether and kept cold it slowly decomposes into the trichloride, imparting the characteristic violet colour to the solution. If an excess of alcohol is added to this solution, some tetrachloride is again formed. Suspended in ether with mercurous chloride it decomposes more rapidly, but all the ordinary reducing agents such as can be used in a solution nearly anhydrous cause immediate decomposition without the intermediate stage. Absolute alcohol seems to be the only solvent which will dissolve the tetrachloride without rapid decomposition. If the alcohol contains a little water the solution is decolorised more quickly.

Summary.

1. When manganese dioxide, suspended in carbon tetrachloride, is acted upon by hydrogen chloride, manganese trichloride and manganese tetrachloride are formed.

2. Manganese trichloride has been isolated and its properties described.

3. When an ethereal solution of manganese trichloride is mixed with a large volume of water only half of the manganese is precipitated.

Analysis I.	Found (grm.).	Calc. (grm.).
Available chlorine	0·0192	—
	0·0192	—
Total chlorine	0·0872	0·0874
	0·0874	0·0850
Chlorine in $MnCl_4$	—	0·0428
	—	0·0389
Chlorine in $MnCl_2$	—	0·0446
	—	0·0461
Precipitated manganese ..	0·0164	—
	0·0151	—
Manganese in $MnCl_2$.. ..	0·0346	—
	0·0358	—
Total manganese	0·0510	—
	0·0509	—

$$\frac{\text{Available chlorine}}{\text{Total chlorine}} = \frac{0·0192}{0·0408} = 0·470.$$

$$\frac{\text{Precipitated manganese}}{\text{Chlorine in } MnCl_4} = \frac{0·0157}{0·0408} = 0·385. \quad \text{Theory, } 0·387.$$

Analysis II.	Found (grm.).	Calc. (grm.)
Available chlorine	0·0059	—
	0·0060	—
Total chlorine	0·0442	0·0440
	0·0442	0·0443
Chlorine in $MnCl_4$	—	0·0140
	—	0·0140
Chlorine in $MnCl_2$	—	0·0300
	—	0·0303
Precipitated manganese ..	0·0054	—
	0·0054	—
Manganese in $MnCl_2$.. ..	0·0233	—
	0·0235	—
Total manganese	0·0287	—
	0·0289	—

$$\frac{\text{Available chlorine}}{\text{Total chlorine}} = \frac{0·0060}{0·0140} = 0·429.$$

$$\frac{\text{Precipitated manganese}}{\text{Chlorine in } MnCl_4} = \frac{0·0054}{0·0140} = 0·386. \quad \text{Theory, } 0·387.$$

4. Manganese tetrachloride has been isolated and its properties described.

5. When an alcoholic solution of manganese tetrachloride is diluted with a large volume of water, all the manganese is precipitated.

6. Manganese tetrachloride is probably the first product formed when manganese dioxide and hydrochloric acid interact.—*Journal of the American Chemical Society*, xxix., No. 9.

OBITUARY.

LORD KELVIN.

With deep regret we chronicle the death, on the 17th inst., of the Right Honourable William Thomson, Baron Kelvin, the last survivor of that band of intellectual giants—Faraday, Darwin, Clerk Maxwell, Joule, Huxley, Lyell—whose achievements shed such glory on the mid-Victorian era.

In the shadow of a great loss it is hard to write dispassionately, but we do not hesitate to say that no man has done more than Lord Kelvin to mould the destinies of his country in those scientific directions which constitute true progress. If we seek to trace out the material steps which during the last half century have placed British science in the first rank, we shall come, in most cases, to a substratum based on and due to an observation of Lord Kelvin's. Few men of his generation have given to the world more discoveries which have ramified in so many directions, or have done so much to advance human welfare.

Lord Kelvin's funeral took place on Monday in Westminster Abbey, in the presence of men of science from all parts of the United Kingdom and the Continent. He was followed to the grave by a numerous company of friends and pupils, where he rests at the feet of his great prototype Newton.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 5th, 1907.

Sir William Ramsay, K.C.B., F.R.S., President, in the Chair.

The President announced that Professor Wislicenus, of Tübingen, was arranging to establish a memorial to the late Professor Lothar Meyer.

Certificates were read for the first time in favour of Messrs. Edward Philip Andreae, Ph.D., Crestalba, Champion Hill, S.E.; Marie Joseph Arsène Braun, Ph.D., 5, Aspinall Road, Brockley, S.E.; William Henry Collier, 13, Powis Gardens, Bayswater, W.; John Maxwell Heron, North House, Manningtree, Essex; Thomas Percy Hilditch, 4, Park Hall Place, E. Finchley, N.; Capet Darcy Morewood, Ferndale, Frodingham, Doncaster; Alfred William Oke, B.A., LL.M., 32, Denmark Villas, Hove; Douglas Robert Pinnoik, 31, The Gardens, E. Dulwich, S.E.; Arthur Robert Runeekles, 68, Kyrle Road, New Wandsworth, S.W.; Adolph Octavius Trechmann, The Old Palace, Rochester; Alfred Wade, Government Pharmacist, Fiji; Herbert Edmeston Watson, B.Sc., Tringhurst, Cranes Park, Surbiton; Harry Percy Wilson, 3, Audley Road, Colchester.

A ballot for the election of Fellows was held, and the following were subsequently declared duly elected:—Arthur John Banks; Edward De Barry Barnett; John Forbes Bell; Frank Buckney, B.A.; Thomas Callan, B.Sc.; Frederic William Caton, B.A., B.Sc.; George Hugh Crisp, B.A.; Edward Henry Croghan; Edward Joseph Day, M.D., M.R.C.S.; Frederick Harold Dupré; Percy Vivian Dupré; Francis Bridger Dutton; Claude Scott Fawcitt; Charles Thomas Foreman; Thomas Rigby Greenough, B.A.; William Hay; William Doge Hutchinson, B.A.; Harry Ingham, M.Sc.; Benjamin Owen Jones; John Kaye, M.A., B.Sc.; Herbert Marsden, B.Sc.; Hubert Frederick Sankey Marshall; Gerald Hargrave Martin; John Edward Langford Moore; Charles Samuel Mummery; George Joseph Saunders, B.E.; William Bush Schober, A.M., B.Sc., Ph.D.; Robert Harry Smith; Harold Ramsay Stobie; Frederick Thomas, B.Sc.; Harold Munkman Timpany, M.Sc.; George Arthur Watson; Marcus Wechsler, D.Sc.; Edward Wheeler; Robert Whymper; Percy Williams, B.Sc.; David Willott, B.Sc.; William John Wilson; Hubert Arthur Wootton, B.A., B.Sc.

Of the following papers, those marked * were read:—

*239. "*The Affinity Constants of Bases as Determined by the Aid of Methyl-orange.*" (Preliminary Note.) By Victor Herbert Veley.

In a former communication (*Trans.*, 1907, xci., 155), it was shown that if x be the units of 0·1 cc. hydrochloric acid added to an $N/40{,}000$ solution of methyl-orange, and y be the heights of a variable tintometer column, expressed in centimetres, required to produce the required match in tint, then $y = kx - b$. In this expression, k is the essential factor (or constant) of y in terms of x and b is accidental.

Certain values of k were obtained for hydrochloric acid, as also for the hydrochlorides of some aminocarboxylic acids.

As it was thought that such values might serve to determine the amount of free hydrochloric acid, and hence the degree of hydrolysis of the hydrochlorides of bases, preliminary experiments were made without any special care with a sample of *m*-phenylenediamine hydrochloride. It was then found with aqueous solutions of this salt containing an equi-acidic quantity of this acid, whether free or combined, that the ratio $k[\frac{1}{2}C_6H_4(NH_2)_2,2HCl]/k_1[HCl] = 0{\cdot}5$ approximately. In other words, 50 per cent of the salt is hydrolysed into the free base and acid. As the result is identical with that obtained by Bredig (*Zeit. Phys. Chem.*, 1894, xiii., 214), it was thought that this very simple line of investigation might be pursued further. So far, the hydrochlorides of about forty bases of various degree of complexity, ranging from hydroxylamine to cinchonidine, have been examined. Several results are found to be in accordance with the expression of Arrhenius $k_b/k_w = (1 - x)v/x^2$ (*Zeit. Phys. Chem.*, 1881, v., 17), even at the great dilutions examined, whilst in the case of bases of analogous composition the ratio of the hydrolysis values found is nearly equal to the ratio of the heats of neutralisation with hydrochloric acid.

*240. "*The Constituents of the Essential Oil of Nutmeg.*" By Frederick Belding Power and Arthur Henry Salway.

The material employed in this investigation consisted of an oil which was distilled from unlimed Ceylon nutmegs of good quality, and was obtained in a yield of 6·94 per cent. It had $d\ 15°/15° = 0{\cdot}8690$; $\alpha_D + 38'\ 4'$ in a 1-dcm. tube; acid value, 0·81; ester value, 3·15. The more complete examination of the oxygenated constituents of the oil was accomplished by means of a product, designated heavy oil of nutmeg, from which the terpenes had been to a large extent removed. This had $d\text{-}20°, 20° = 1{\cdot}102$; $\alpha_D + 1°\ 17'$ in a 1-dcm. tube; saponification value, 6·10.

This investigation has shown that the essential oil of nutmeg contains the following substances:—(1) eugenol and (2) *iso*eugenol (about 0·2 per cent); (3) *d*-pinene and (4) *d*-camphene (about 80 per cent); (5) dipentene (about 8 per cent); (6) *d*-linalool, (7) *d*-borneol, (8) *i*-terpineol, and (9) geraniol (about 6 per cent); (10) a new *alcohol*, yielding on oxidation a *diketone*, $C_8H_{14}O_2$ (a very small amount); (11) a trace of an *aldehyde* resembling citral, but yielding a *β-naphthacinchoninic acid* derivative melting at 248°; (12) safrole (about 0·6 per cent); (13) myristicin, $C_{11}H_{12}O_3$ (about 4 per cent); (14) myristic acid, in a free state (about 0·3 per cent), and apparently a small amount in the form of esters; (15) formic, acetic, butyric, and octoic acids, and a new *monocarboxylic acid*, $C_{13}H_{18}O_3$, all in the form of esters, and in relatively small amount.

This investigation has also shown that the portion of nutmeg oil which has hitherto been designated "myristicol" is a mixture of alcohols, of which terpineol appears to be the predominating constituent.

Discussion.

Dr. Wade remarked that none of the constituents which had been isolated seemed to possess the characteristic odour of nutmeg, and asked whether the authors had been able to trace this odour to its source.

Dr. Power stated that the characteristic odour of nutmeg oil is not that of any individual substance, but is due to the mixture of odorous compounds contained in the oil.

*241. "*The Resolution of* sec.*-Octyl Alcohol (Methylhexylcarbinol Octane-2-ol).*" By Robert Howson Pickard and Joseph Kenyon.

sec.-Octyl alcohol is readily converted into the acid phthalic ester. The dextro-sec.-*octyl hydrogen phthalate* is then obtained by the fractional crystallisation of its *brucine* salt from acetone, and the corresponding *lævo*-compound by the fractional crystallisation of the *cinchonidine* salt from aqueous acetone.

The *sec.*-octyl hydrogen phthalates have $[\alpha]_D$ 48·2° in ethyl-alcoholic solution, and when hydrolysed yield the pure alcohols which have $[\alpha]_D$ 17° 9·87°.

242. "*The Velocity of Reduction of the Oxides of Lead, Cadmium, and Bismuth by Carbon Monoxide, and the Existence of the Suboxides of these Metals.*" By Francis Joseph Brislee.

The production of lead, cadmium, and bismuth suboxides by the reduction of the higher oxides with carbon monoxide has been investigated. The velocity of reduction of the oxides was determined by heating the oxides, contained in a porcelain boat, to 300° in an apparatus in which carbon monoxide was circulated. The boat was withdrawn from

time to time and the loss in weight observed. The time interval varied from one and a-half to six hours. The results were then plotted as time-reduction curves, and these showed a distinct break at the point at which the analytical composition of the product was near that required for the suboxide. The position of the break was not always at the suboxide point, the position depending on the relative velocities of the two reductions, namely :—

1. Oxide → suboxide.
2. Suboxide → metal.

When the velocity of 1 is very different from 2, then the break will occur at the point when the oxide is entirely reduced to suboxide. When these two velocities are not very different, the first stage of the reduction is—

(1*a*) Oxide → suboxide → metal,

and the second is—

(2*a*) Suboxide → metal,

and then the break will occur below the point, corresponding to complete reduction of the oxide to suboxide. The experiments made on the velocity of reduction of the oxides of lead, cadmium, and bismuth confirm Tanatar's results (*Zeit. Anorg. Chem.*, 1901, xxvii., 304) that the suboxides of these metals are definite chemical compounds, but do not prove the stability of these compounds. The suboxides of lead, cadmium, and bismuth are formed as intermediate phases in the reduction of the oxide to metal by carbon monoxide.

243. "*The Relation between Unsaturation and Optical Activity.* Part I. *The Menthyl and Bornyl Esters of β-Phenylpropionic, Cinnamic, and Phenylpropiolic Acids.*" By Thomas Percy Hilditch.

In order to throw further light on Walden's statement that increase of unsaturation in a compound is accompanied by increase in rotatory power, the author has prepared and investigated the properties of the menthyl and bornyl esters of the above three acids. Menthyl hydrocinnamate (m. p. 28°), menthyl phenylpropiolate (m. p. 33°), and bornyl phenylpropiolate (m. p. 45°) were obtained as nearly colourless, crystalline solids, whilst the other three esters were found to be liquid at the ordinary temperature. The boiling-points of the compounds, as well as the specific gravities, seems to show a regular increase with increase of unsaturation, whilst the refractive indices rise with a change to an ethylenic linking, but fall to an intermediate value for the further change to an acetylenic compound.

The following conclusions were arrived at as regards optical activity :—

1. The change in rotation for either change of constitution is relatively small.

2. The changes are nevertheless perfectly definite, and occur in a regular manner for corresponding stages of unsaturation (the rotations being measured at three successive concentrations in each of two solvents, chloroform and acetone).

3. The conversion of a saturated to an ethylenic bond is accompanied by an increase in optical activity, whilst the change from a saturated to an acetylenic linking produces a decrease in rotatory power.

4. In the case of esters, the change in rotation must be measured with reference to the difference between the specific rotation of the ester and that of the active alcohol from which it was formed.

5. Walden's results are confirmed so far as the change to an ethylenic linking is concerned, but there is a discrepancy with regard to the influence of the triple bond on the optical activity.

244. "*Methyl Ethers of some Hydroxyanthraquinones.*" By Arthur George Perkin.

The author has re-examined the principal non-tinctorial derivatives of anthraquinone present in Chay-root, *Oldenlandia umbellata* (Perkin and Hummel, *Trans.*, 1893, lxiii., 1160, and 1895, lxvii., 817), and finds, contrary to the suggestion of Böck (*Monatsh.*, 1902, xxiii., 1008), that these compounds possess the constitution previously assigned to them, and do not contain reduced anthraquinone nuclei. The anthragallol dimethyl ether (A), m. p. 209°, when treated with alcoholic potassium acetate, gives the salt, $C_{16}H_{11}O_5K$, in violet-coloured leaflets, and on methylation forms *anthragallol trimethyl ether*, which crystallises in pale yellow needles, m. p. 167—168°. Anthragallol dimethyl ether (B) on methylation gives the same trimethyl ether, but the melting-points of this dimethyl ether and its acetyl derivative, previously given as 225—227° and 175° respectively, are now found to be 230—232° and 176—178°. Experiments indicate that, whereas in the compound (A) the methoxy-groups are present in the positions 1 : 3, in (B) they occupy the positions 1 : 2. Alizarin *a*-methyl, ether, m. p. 177—179°, on methylation gives alizarin dimethyl ether, m. p. 210—211°, and its acetyl compound, m. p. 212°, contains only one acetyl group. With potassium acetate, it gives a potassium salt, which forms garnet-red prismatic needles.

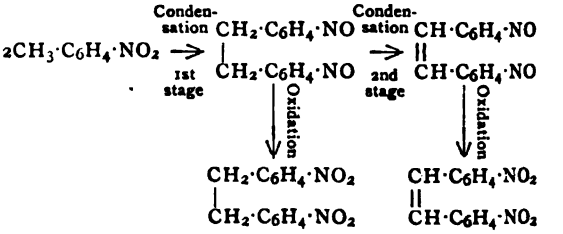
Hystazarin monomethyl ether on methylation gives *hystazarin dimethyl ether*, yellow needles, m. p. 235—236°, identical with the compound prepared from hystazarin itself. Finally, the natural *m*-hydroxyanthraquinone gave the methyl ether m. p. 192—193°. The so-called anthragallol dimethyl ether (C) was previously isolated in so small an amount that it could not be profitably re-examined, but, as the description of Böck's dimethyl ether (*loc. cit.*), does not agree with that assigned to this compound, it is possibly not a distinct substance.

A re-examination of emodin monomethyl ether (Perkin and Hummel, *Trans.*, 1894, lxv., 923) has confirmed the properties, melting-point, &c., previously assigned to it, so that Oesterle's conjecture that it is identical with his trihydroxymethylanthraquinone monomethyl ether (*Arch. Pharm.*, 1907, ccxlv., 287) is incorrect.

245. "*The Colouring Matters of the Stilbene Group.* Part IV. *Action of Caustic Alkalis on Para-nitrotoluene and its Derivatives.*" By Arthur George Green, Arthur Hugh Davies, and Ronald Smith Horsfall.

The authors find that the product of oxidation of substituted *p*-nitrotoluenes under the influence of caustic alkalis is largely dependent on the reactivity of the particular compound employed, this being determined by the nature of the ortho-substituent. Thus, whilst the cyano-derivative (like the chloro-derivative and the phenyl sulphonate already investigated) gave only a stilbene derivative, dibenzyl compounds were obtained from the methyl, methoxy-, and carboxy-derivatives, and both stilbene and dibenzyl derivatives from *p*-nitrotoluene itself. Those derivatives which react least easily with production of red condensation products yield dibenzyl compounds by preference, whilst those which react most readily and form violet to blue condensation products give chiefly stilbene compounds.

The results point to the conclusion that the condensation in question occurs in two stages, which may be more or less concurrent according to the degree of reactivity of the substance. The product of the first stage, when oxidised, gives a dinitrodibenzyl, that of the second stage a dinitrostilbene :—



Substituents which increase the reactivity of the substance therefore favour the formation of stilbene compounds.

A comparison of the relative reactivity of a number of such compounds under like conditions shows that, whilst the methyl, methoxy-, amino-, and carboxy-groups have

but little influence on the reactivity, the more strongly electro-negative groups, such as the sulphophenyl, cyano-, and nitro-groups, exert a powerful effect, that of the nitro-group being the strongest.

246. "*The Replacement of Alkyl Radicles by Methyl in Substituted Ammonium Compounds.*" By HUMPHREY OWEN JONES and JOHN ROBERTSHAW HILL.

It has been shown previously (*Proc.*, 1901, xvii., 205; *Trans.*, 1905, lxxxvii., 1726) that the allyl and benzyl groups are readily displaced from amines or quaternary ammonium compounds by the methyl group on treatment with methyl iodide either at the ordinary temperature or at 100°.

The authors now find that the other alkyl groups, ethyl, propyl, *iso*propyl, butyl, *iso*butyl, and *iso*amyl, are all replaced by methyl, sometimes in the cold, but more easily on heating with methyl iodide.

The two series of ammonium compounds derived from dimethylaniline and *p*-bromodimethylaniline (Hill, *Proc. Camb. Phil. Soc.*, 1907, xiv., 166) have been examined, and the phenyltrimethyl compound is the final product in each case. The replacement is due to the dissociation of the ammonium salt, in methyl iodide solution, into tertiary amine and alkyl iodide, the tertiary amine then combines with methyl iodide to produce the trimethyl compound, which is, in each case, much the least soluble of all. The ease with which the different groups are replaced varies considerably, and is dependent jointly on the extent to which the dissociation takes place and on the solubility of the ammonium salt. The ethyl or *iso*butyl group is most readily replaced, and the *iso*amyl group is the most difficult to displace.

247. "*Note on the Formation of Abnormal Platinichlorides.*" (A Correction). By ALBERT ERNEST DUNSTAN.

In a recent communication (Dunstan and Cleaverley, (*Trans.*, 1907, xci., 1619), the preparation of three platinichlorides of the general formula B_4,H_2PtCl_6 was described. These were thought to belong to a new type of platinichlorides, but this is now found to be a mistake, as Werner (*Ber.*, 1903, xxxvi., 147) had collected all instances of such abnormalities known up to that date. Subsequently, Morgan and Micklethwait (*Trans.*, 1906, lxxxix., 863) added the cases of coumarin platinichloride and aurichloride, whilst Pickard and Kenyon have described (*Trans.*, 1906, lxxxix., 268) triethyl-, tripropyl-, and tribenzylphosphine oxide hydrogen platinichlorides, the latter of which had been prepared by Fleissner (*Ber.*, 1880, xiii., 1665), and by Letts and Collie (*Trans. Roy. Soc. Edin.*, 1888, xxx., I., 181).

248. "*The Nitrates of Dimethyl- and Methylethylthetine Menthyl Esters.*" By SAMUEL SMILES.

The nitrates of dimethyl- and methylethyl-thetine menthyl esters were prepared by precipitating concentrated aqueous solutions of the bromides with aqueous ammonium nitrate. *Dimethylthetine* l-*menthyl ester nitrate* forms colourless prisms which melt at 125—127°, and are very sparingly soluble in cold water or ethyl acetate, but readily so in the hot media. In alcoholic solution (1) 2 per cent the salt has $[\alpha]_D - 53{\cdot}9°$ and $[M]_D - 173°$ approximately. *Methylethyl*-d-l-*thetine* l-*menthyl ester nitrate* has $[M]_D$ about $-178°$ in the same solvent; it melts at 120—122°, and is slightly more soluble than the dimethyl derivative.

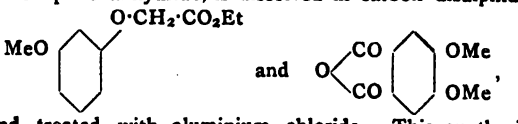
The methylethyl salt was fractionally crystallised from ethyl acetate with a view to resolving the thetine into optical isomerides. The experiments have been hitherto unsuccessful, probably owing to the instability of the ester to which attention has already been drawn (*Trans.*, 1905, lxxxvii., 451). The less soluble fraction contained the dimethylthetine ester, indicating the decomposition of the salt. The rotatory powers of the plantinichlorides of the dimethyl and methylethyl derivatives are corrected from these already given to $[M]_D - 438°$ for the dimethyl and $[M]_D - 380°$ approximately for the methylethylthetine, that for the diethyl being, as before, $[M]_D - 330°$.

249. "*Synthesis of Brazilinic Acid and the Lactones of Dihydrobrazilinic and Dihydrohæmatoxylinic Acids.*" (Preliminary Note). By WILLIAM HENRY PERKIN, jun., and ROBERT ROBINSON.

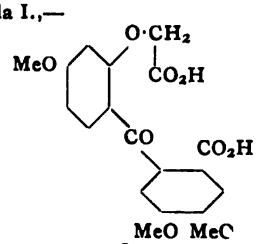
Brazilinic acid is formed when trimethylbrazilin is oxidised by permanganate (*Trans.*, 1902, lxxxi., 1030), $C_{19}H_{20}O_5 + O_5 = C_{19}H_{18}O_9 + H_2O$, and, on reduction, is converted into the lactone of dihydrobrazilinic acid, $C_{19}H_{18}O_9 + 2H = C_{19}H_{18}O_8 + H_2O$.

Since these two acids contain the same number of carbon atoms as trimethylbrazilin, it seemed probable that the determination of their constitutions might yield information which would definitely prove the constitution of brazilin. The authors have succeeded in synthesising brazilinic acid, the lactone of dihydrobrazilinic acid, and also the corresponding lactone of dihydrohæmatoxylinic acid by methods which leave no doubt as to their constitutions.

Brazilinic acid (m. p. 208°) is obtained in small quantity when a mixture of *m*-methoxyphenoxyacetic ester and *m*-hemipinic anhydride, is dissolved in carbon disulphide

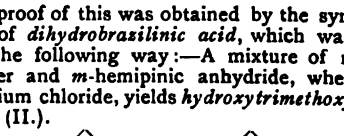


and treated with aluminium chloride. This synthesis clearly indicated that brazilinic acid must be represented by the Formula I.,—



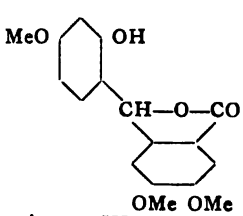
I.

and further proof of this was obtained by the synthesis of the *lactone* of *dihydrobrazilinic acid*, which was accomplished in the following way:—A mixture of resorcinol dimethylether and *m*-hemipinic anhydride, when treated with aluminium chloride, yields *hydroxytrimethoxybenzoylbenzoic acid* (II.).

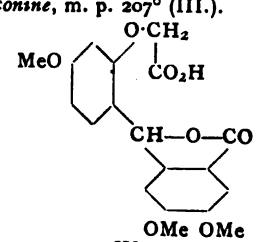


II.

Reduction with sodium amalgam converts this acid into *hydroxymethoxyphenyl*-m-*meconine*, m. p. 207° (III.).



III.

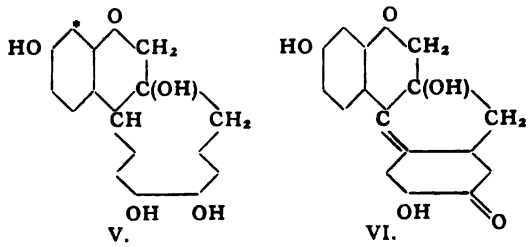


IV.

When this substance is treated with chloroacetic acid and potassium hydroxide, it is converted into an acid which melts at 226—227°, and is identical with the *lactone* of *dihydrobrazilinic acid*.

The latter acid must therefore have the constitution IV.

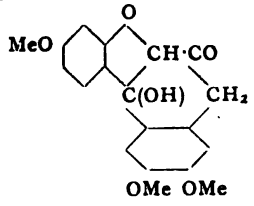
This synthesis not only confirms the constitution given above to brazilinic acid, but the authors consider that it proves clearly that brazilin must be represented by the constitutional formula V., first suggested by Werner and Pfeiffer (*Chem. Zeit.*, 1904, iii., 421).



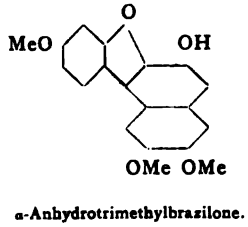
V. VI.

The *lactone* of *dihydrohæmatoxylinic acid* (m. p. 192°) was similarly synthesised from pyrogallol trimethyl ether and *m*-hemipinic anhydride by treatment with aluminium chloride and subsequent reduction and treatment with potassium hydroxide and chloroacetic acid. The constitution for hæmatoxylin is therefore derived from the above formula for brazilin by the introduction of a hydroxy-group at the point indicated by the asterisk.

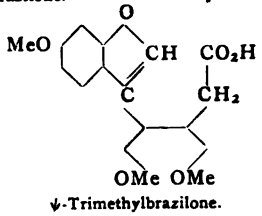
An entirely different series of experiments on brazilein, carried out in conjunction with Paul Engels, has shown that the constitution of this important substance is represented by VI., an expression easily derived from the formula of brazilin given above. In the detailed account of the authors' experiments, it will be further shown that the important derivatives of trimethylbrazilin, namely, trimethylbrazilone, *a*-anhydrotrimethylbrazilone, and ψ-trimethylbrazilone, have constitutions represented by the formulæ :—



Trimethylbrazilone.



a-Anhydrotrimethylbrazilone.



ψ-Trimethylbrazilone.

250. "*Condensations of Ketones containing the Group* $\cdot CH_2 \cdot CO \cdot CH$: *with Esters in presence of Sodium Ethoxide.*" By Reginald William Lane Clarke, Arthur Lapworth, and Elkan Wechsler.

It has already been shown (*Trans.*, 1907, xci., 1919) that when cyanodihydrocarvone, which contains the above grouping, is acted on by nitrous esters in presence of sodium ethoxide, the attack occurs at the $\cdot CH$: group. It is now proved that menthone reacts in the same way, although when alkyl formates are used under analogous conditions it is the $\cdot CH_2 \cdot$ group which is reactive. Pulegone appears first to be converted into *iso*pulegone, which then behaves like menthone, yielding a *hydroximino-acid* having the structure :—

$$\begin{matrix} CH_3 \\ CH_2 \end{matrix} \geqslant C \cdot C(:NOH) \cdot CH_2 \cdot CH_2 \cdot CH(CH_3) \cdot CH_2 \cdot CO_2H.$$

Bromocamphor yields only *iso*nitrosocamphor, and fenchone, in accordance with Semmler's view of its constitution, is quite unaffected.

The fact that esters of different kinds, acting under the influence of sodium ethoxide and similar agents, appear to select different points for attack on ketones containing the group $\cdot CH_2 \cdot CO \cdot CH$:, is shown to be of considerable importance in connection with the question of the mechanism of syntheses brought about by such agents.

251. "*Acylogens and Thiocarbamides.*" By Augustus Edward Dixon and John Taylor.

Following up their previous inquiries in the above direction (*Trans.*, 1907, xci., 912; compare also Dixon and Hawthorne, *Ibid.*, 122), the authors have now studied the behaviour of certain acyl chlorides with allyl-substituted thiocarbamides, and of phenylthiocarbamide with halogenised acyl halides.

Acetyl chloride unites with allylthiocarbamide to form $C_3H_5 \cdot NH \cdot C(NH) \cdot SAc,HCl$, white crystals, melting at 103—104°. On withdrawal of the combined halogen acid by weak alkali, the acetyl group migrates with production of $C_3H_5 \cdot NAc \cdot CS \cdot NH_2$, m. p. 96°, the latter, when melted, undergoing further change into $C_3H_5 \cdot NH \cdot CS \cdot NHAc$, m. p. 74°; of these three isomeric forms, the first alone is basic.

With *ab*-phenylallylthiocarbamide, acetyl chloride yields N-phenylpropylene-ψ-thiourea (Prager, *Ber.*, 1889, xxii., 2992).

Methyl chlorocarbonate gives with *ab*-phenylallylthiocarbamide the compound $C_3H_5 \cdot NH \cdot C(NPh) \cdot S \cdot CO_2Me,HCl$ (m. p. 87°); from this, water eliminates the halogen acid, and the carboxymethyl group thereupon migrates to form $C_3H_5 \cdot N(CO_2Me) \cdot CS \cdot NHPh$, m. p. 83°. Ethyl chlorocarbonate behaves similarly, the hydrochloride melting at 96°, and yielding by treatment with water the corresponding trisubstituted thiocarbamide as a non-basic oil.

Chloroacetyl chloride and bromopropionyl bromide react readily with phenylthiocarbamide, but not to produce additive compounds; instead, two molecules of halogen acid are eliminated, one of which passes off, the other remaining combined with the product, a ring compound, either "phenylthiohydantoin," $PhN:C\begin{matrix} NH \cdot CO \\ | \\ S—CH_2 \end{matrix}$, or its methylic homologue, as the case may be.

Acetyl chloride combines with benzyl-ψ-thiourea, $NH_2 \cdot C(NH) \cdot S \cdot CH_2Ph$, furnishing the hydrochloride of an acetyl derivative, and, conversely, benzyl chloride unites additively with acetylthiocarbamide; whether the products are identical or isomeric could not be decided owing to the readiness with which they decompose, yielding benzyl mercaptan.

252. "*The Alkyl Compounds of Gold.*" By William Jackson Pope and Charles Stanley Gibson.

The authors have prepared *monoethylauric dibromide*, $(C_2H_5)AuBr_2$, and *amminodiethylauric bromide*, $(C_2H_5)_2AuBr,NH_3$ (compare also *Proc.*, 1907, xxiii., 245).

253. "*The Refractive Power of Diphenylhexatriene and Allied Hydrocarbon.*" By Ida Smedley.

The molecular refractions of diphenylbutadiene and diphenylhexatriene (*Proc.*, 1907, xxiii., 162) were measured and compared with those of other hydrocarbons. Sufficient data have been obtained to calculate the influence of the phenyl and the ethenoid groups in unsaturated hydrocarbons. In each case, the refractive power of the group increases markedly as the number of unsaturated groups with which it is conjugated increases. The influence of the hexatriene structure is always greater than that of the benzene ring, a result considered by the author to be at variance with the representation of the benzene molecule as a closely conjugated system of double bonds.

MEETINGS FOR THE WEEK.

Tuesday, 31st. Thursday, Jan. 2nd. Saturday, „ 4th.	Royal Institution, 3. (Christmas Lectures, adapted to a Juvenile Auditory). "Astronomy, Old and New," by Sir David Gill, K.C.B., F.R.S., &c.

Royal Institution.—On Saturday next, December 28th, at 3 o'clock, Sir David Gill will deliver the first of the annual course of Juvenile Lectures at the Royal Institution on "Astronomy, Old and New" (illustrated). The remaining lectures will be delivered on December 31st, and January 2nd, 4th, 7th, and 9th.

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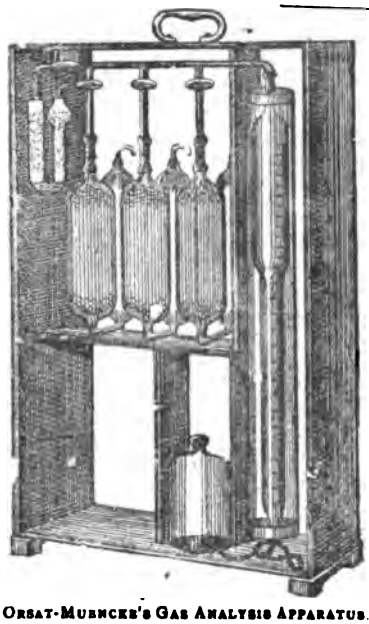

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